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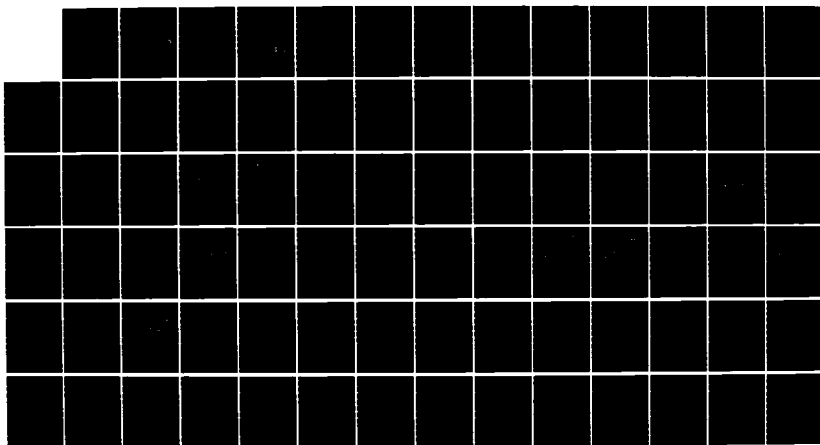
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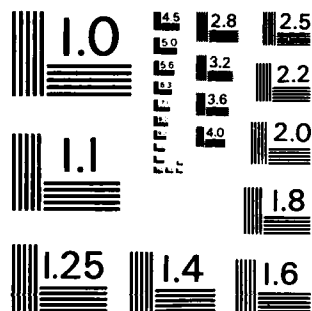
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liquid in a manner parallel to that observed for structurally analogous Dansyl derivatives in solution. Fluorescence was quenched by strongly acidic aqueous media (pH 0-2). Fluorescence quenching by acid correlates with changes in the contact angle of the aqueous solutions on the Dansyl-containing surfaces; this correlation implies a significant concentration of Dansyl groups in the region of the functionalized interphase sensed by contact angle measurements. The position and relatively narrow width of the fluorescence indicate that a majority of the Dansyl groups are located in a uniform environment having a low dielectric constant. Modification of the composition and structure of the Dansyl-containing interphase was accomplished by incorporating into it functional groups (e.g. sulfonate and ammonium) having different polarities and by changing the structure of the group which connects the Dansyl moieties to the polymer. Examination of the fluorescence of these modified films provides additional information concerning the structure and properties of the functionalized interphase.

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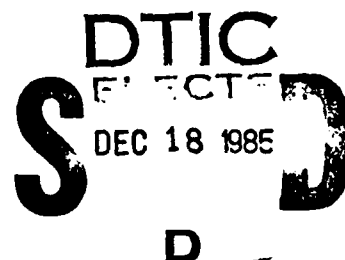
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to the Surface of Oxidatively Functionalized Low-Density
Polyethylene Film

by

Stephen Randall Holmes-Farley and George M. Whitesides

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Fluorescence Properties of Dansyl Groups Covalently Bonded to the Surface of
Oxidatively Functionalized Low-Density Polyethylene Film¹

Stephen Randall Holmes-Farley² and George M. Whitesides*

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Abstract. We have attached the fluorophoric Dansyl (5-dimethylamino-naphthalene-1-sulfonyl) moiety to carboxylic acid groups introduced onto the surface of low-density polyethylene film by reaction with aqueous chromic acid, and used it as a reporter to explore the functionalized interphase between these films and liquids. The Dansyl group was chosen because its fluorescence emission maximum and quantum yield are sensitive to the polarity and acidity of the local environment. The functionalization procedure used introduced $\sim 6 \times 10^{14}$ Dansyl moieties cm^{-2} of geometric film surface. The shape of the fluorescence curves and the similarity of the width of curves of surface-attached dansyl groups to those of soluble analogs suggests that the majority of the surface-bound species experience a common environment, although certain features of the data suggest a second minority population having a different environment. The wavelength of maximum fluorescence depended only weakly on the character of the contacting liquid phase; the difference between cyclohexane and water was approximately 10 nm (from ~ 490 to 500 nm). The fluorescence intensity varied slightly with liquid in a manner parallel to that observed for structurally analogous Dansyl derivatives in

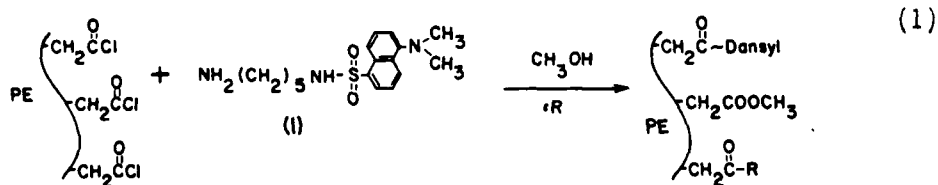
solution. Fluorescence was quenched by strongly acidic aqueous media (pH 0-2). Fluorescence quenching by acid correlates with changes in the contact angle of the aqueous solutions on the Dansyl-containing surfaces; this correlation implies a significant concentration of Dansyl groups in the region of the functionalized interphase sensed by contact angle measurements. The position and relatively narrow width of the fluorescence indicate that a majority of the Dansyl groups are located in a uniform environment having a low dielectric constant. Modification of the composition and structure of the Dansyl-containing interphase was accomplished by incorporating into it functional groups (e.g. sulfonate and ammonium) having different polarities and by changing the structure of the group which connects the Dansyl moieties to the polymer. Examination of the fluorescence of these modified films provides additional information concerning the structure and properties of the functionalized interphase.

Introduction

Brief oxidation of low-density polyethylene film with chromic acid in aqueous sulfuric acid introduces carboxylic acid and ketone and/or aldehyde groups onto the surface of the film.³⁻⁵ The carboxylic acid moieties can be used to attach more complex functionality to the polymer surface. We are developing this surface-functionalized polyethylene (named "polyethylene carboxylic acid," PE-CO₂H, to emphasize the functional group that dominates its surface properties) as a substrate with which to study problems in organic surface chemistry--especially wetting, polymer surface reconstruction, and adhesion--using physical-organic techniques. This manuscript describes the preparation, characterization, and fluorescence properties of derivatives of PE-CO₂H in which the Dansyl (5-dimethylaminonaphthalene-1-sulfonyl) group has

been covalently attached by amide links to the surface carbonyl moieties. This work had three objectives: first, to characterize the surface/interface/interphase of PE-CO₂H and its derivatives and to examine the chemistry of the functionalized surface interphases of these materials; second, to develop synthetic techniques useful in forming derivatives of PE-CO₂H; third, to extend the use of the Dansyl moiety as a fluorophoric reporter group in polymer surface chemistry. We emphasize, as previously,³ that we use the phrase "polymer surface" as shorthand for "oxidatively functionalized polymer interfacial layer," and that a long-term objective of the work is to help to define the structure of this interfacial layer and the extent to which it can be used to study interfacial phenomena.

The synthetic basis for the work is the facile conversion of PE-CO₂H to materials having more complex functionalities covalently attached to the surface via amide or ester linkages. Eq 1 illustrates the reaction of a nucleophilic derivative of Dansyl--Dansyl cadavarine, 1--with the acid chloride PE-COCl derived from PE-CO₂H by treatment with PCl₅. Dansyl can be easily attached to the polymer surface using this type of coupling reaction and linking groups having a wide variety of structures. The fluorescence



maximum and quantum yield of the Dansyl group depend strongly on its microenvironment, especially polarity.^{6,7} This dependence has been carefully characterized and widely applied in studies of soluble Dansyl derivatives,^{6,7} and of Dansyl groups on proteins,^{8,9} in liposomes and micelles,^{10,11} and in polymers.^{12,16} The wavelength of fluorescence emission (λ_{max}) correlates approximately with the dielectric constant of the solvent (and other measures of solvent polarity⁶) because the polar excited state is stabilized by polar solvents. The quantum yield Φ for fluorescence ranges from $\Phi > 0.70$ in hydrocarbon solvents to $\Phi = 0.068$ in water; the reasons for this variation are complex and only partly understood.^{6,7} The fluorescence of the Dansyl group is quenched in media sufficiently acidic to protonate its dimethylamino group. By comparing the fluorescence of Dansyl groups covalently attached to the surface of polyethylene with that of structurally analogous soluble derivatives in homogeneous solution, we expected to be able to infer characteristics of the polymer surface. Related applications of the Dansyl group in studying polymer microstructure have been described before.^{5,6} The ability to vary the nature of the group linking the Dansyl moiety to the surface, and to change the structures and properties of other organic groups present on the surface (represented by R in eq 1) gives a mechanistically useful degree of control in the system.

The chemistry of organic surfaces has been less extensively developed than the chemistry of metal and metal oxide surfaces. Because the underlying organic solids are often non-crystalline, heterogeneous, and swollen by contact with liquids^{13,14} a number of persistent ambiguities limit the detail in which the experimental data can be interpreted. Our previous studies of PE-CO₂H have established that carboxylic acid groups and ketones (and possibly aldehydes) are the only significant oxygen-containing functionalities present

on the polymer surface.³⁻⁵ All (>95%) of the carboxylic acid groups are neutralized on exposure to aqueous base; none (within our detection limits) are so buried in the polymer interior that they are isolated from proton-transfer equilibrium involving the solution. All presently available experimental data are compatible with (but do not rigorously demand) that the carboxylic acid groups occupy a thin surface layer also containing ketones, methyl and methylene units and solvent. The functionalized surface is stable at room temperature: carboxylic acid groups do not spontaneously migrate into the polymer interior on standing, although such migration is rapid at temperatures close to the melting point of the polymer (~100-130 °C). The surface resists contamination by trace adsorbates present in the laboratory atmosphere or solution, and is readily cleaned if contaminated. Present evidence concerning PE-CO₂H has not resolved questions of microscale morphology for the functionalized surface, of the specific distribution of functional groups at the surface or in the functionalized interphase region, of differences in the chemistry of carboxylic acid groups associated with crystalline and amorphous regions of the polymer, or of the stability of the surface to certain types of conditions used in chemical modification of carboxylic acid groups.

This work emphasizes attachment of organic moieties in the functionalized interphase of PE-CO₂H by formation of amide and ester groups (from PE-COCl). We emphasize that other types of coupling chemistry may also be involved, reflecting reaction of the ketone moieties present in PE-CO₂H with PCl₅ and amines. We have not explicitly examined the importance of these types of reactions, but we note that they are undoubtedly less important than reactions involving acid chloride moieties, and that, in any event, the nature of the group linking the dansyl moiety to the surface has little influence on its fluorescence.

Results

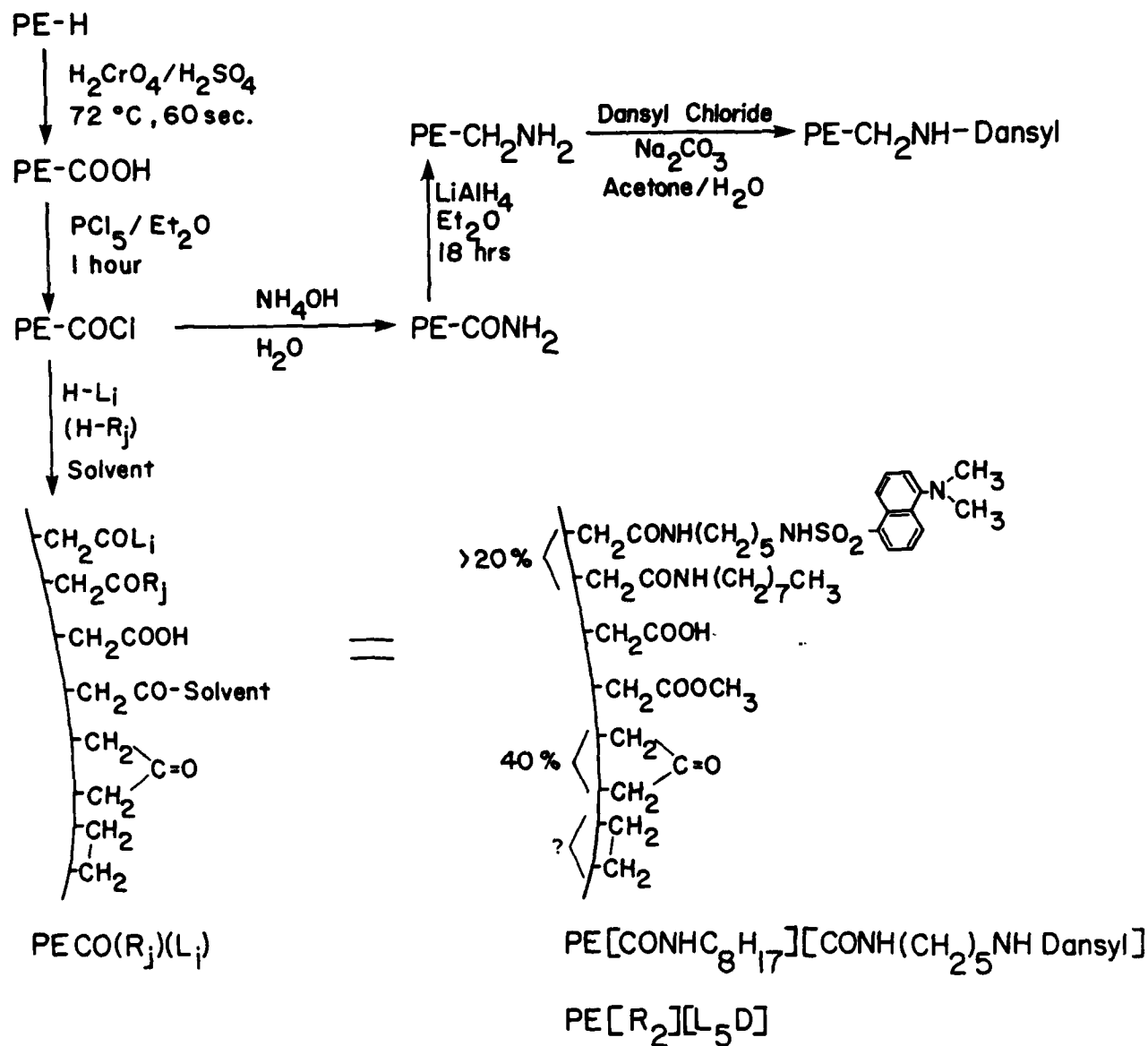
Preparation of Derivatives of PE-CO₂H: General Methods. This work has relied primarily on reactions that generate derivatives of PE-CO₂H by forming amides and esters. We have emphasized chemistry based on acid chlorides and active esters because we required synthetic methods that proceed in good yield under mild conditions, and that permit the composition of the surface to be varied widely and conveniently. Scheme I outlines the synthetic methods followed.

The density of surface carboxylic acid groups on PE-CO₂H is $\sim 1.6 \times 10^{15} \text{ cm}^{-2}$ of geometrical film area (that is, the area calculated assuming the polymer surface to be flat, and thus uncorrected for microscopic surface roughness).³ For comparison, a close-packed monolayer of carboxylic acid groups in crystalline stearic acid or in a Langmuir-Blodgett film has a functional group density of $\sim 5 \times 10^{14} \text{ cm}^{-2}$.¹⁵ The roughness factor for the oxidized polyethylene surface is not known, but is at least ~ 2 -4 and is probably greater: the measured density of carboxylic acid groups on the polymer is therefore less than $4\text{-}8 \times 10^{15} \text{ cm}^{-2}$. We believe, but have not proved, that the oxidation reaction used to generate functionality in the conversion of polyethylene to PE-CO₂H does not introduce branches into the carbon backbone of the polymer. Thus, to a first approximation, the number of carboxylic acid groups per unit area of surface of PE-CO₂H should be no greater than (and may be significantly less than) the number of carbon chains per unit area. The uncertainty in the surface roughness of PE-CO₂H and in the three-dimensional distribution makes it impossible for us to estimate quantitatively the surface density of carboxylic acid groups for this material. We note, however, that the hydrophilicity of the surface of PE-CO₂H is intermediate between that of unfunctionalized polyethylene and model surfaces (see below) made up of monolayer films containing a high density of carboxylic acid groups. Thus, for example, the advancing contact angle (θ_a) of water (pH 3) on polyethylene itself is $\theta_a = 103^\circ$; that on PE-CO₂H is $\theta_a = 55^\circ$; and

that on monolayer films having closely packed terminal carboxylic acid groups is $\theta_a \pm 0^\circ$.¹⁶ Based on this type of evidence, we believe that no more than 30% of the organic groups exposed on the surface of PE-CO₂H are CO₂H groups; the remainder are ketone (aldehyde) and methylene (methyl) moieties.³

The conversion of PE-CO₂H to PE-CO₂CH₃ is complete (within our limits of detection: >95%), using the transformations shown in Scheme 1.³ Figure 1 summarizes ATR-IR evidence relevant to the characterization of PE-CO₂H and its derivatives. The techniques used to obtain these spectra are discussed in greater detail elsewhere³; we make only summary comments here. First, the conversion of surface carboxylic acid groups to surface carboxylate ions can be accomplished by treatment with aqueous base (pH 13). With appropriate experimental precautions, it is possible to prepare samples suitable for infrared analysis in which this conversion is complete. The ability to shift the carbonyl adsorption frequency of surface CO₂H groups selectively by treatment with base while leaving other carbonyl-containing groups unaffected is very useful in characterization of the functionality present on the surface of derivatives of PE-CO₂H. The only important infrared-active contaminants present on the surface of PE-CO₂H are ketone groups (and perhaps aldehyde groups). The characteristic frequencies of these functionalities, and of ester and amide functionalities introduced during derivatization of PE-CO₂H, are all invariant to changes in pH.

The ketone/aldehyde groups can be selectively reduced to alcohols by treatment with borohydride ion (Figure 1).³ The carbonyl region of borohydride-treated PE-CO₂H is simpler than that of PE-CO₂H itself, in that the only carbonyl groups present are carboxylic acid groups, and these are easily identified by their shift in frequency on treatment with base. In general, we have not bothered to reduce the ketone groups with borohydride,



Scheme 1. Reactions Used to Modify the Surface of Polyethylene. The schematic structures for $\text{PE[R}_2\text{][L}_5\text{D]}$ suggest the range of groups present in the functionalized interphase, and illustrate the nomenclature used for these materials.

Figure 1. ATR-IR spectra of the carbonyl region of PE-CO₂H and derivatives. The frequencies indicated are those used in identifying the carbonyl-containing functional groups of major interest: carboxylic acid and ketone (1710 cm⁻¹); methyl ester (1740 cm⁻¹); carboxylate ion (1560 cm⁻¹); and amide (1660 cm⁻¹). The spectrum labeled PE-H; PCl₅; CH₃OH is a control demonstrating that polyethylene that has not been oxidatively functionalized does not develop carbonyl functionality using the succession of treatments used to convert PE-CO₂H to PE-COCl and thence to PE-CO₂CH₃. The spectra taken at pH 13-14 and used to identify free carboxylic acid groups on the basis of the characteristic shift between CO₂H and CO₂⁻ were obtained with procedures outlined previously.³

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and have relied on infrared analysis (specifically the intensity of carboxylate ion absorption at 1560 cm^{-1} in IR spectra taken of films neutralized with base) to confirm the extent of conversion of carboxylic acid to amide or ester moieties during a reaction sequence. For example, the spectra in Figure 1 indicate that for PE-CO₂H, after conversion of surface carboxylic acid groups to acid chlorides with PCl₅ and subsequent reaction with methanol to form methyl esters, no carboxylate functionality is detectable by ATR-IR of films following treatment with aqueous base at pH 13; our experimental procedures would detect less than 10% of unreacted CO₂H groups. Control experiments with unoxidized polyethylene establish that this procedure does not itself oxidize the film nor introduce spurious carboxylic acid, acid chloride, or ester functionalities. We conclude from these studies that the conversion of surface carboxylic acid groups to surface acid chloride functionalities on treatment with PCl₅ is effectively quantitative (i.e. greater than 90-95%, our limit of detection) and that conversion of these surface acid chlorides to esters and amides can also proceed in high yield under appropriate reaction conditions. This procedure does, however, leave appreciable quantities of phosphorus in the functionalized interphase (see below).

X-Ray photoelectron spectroscopy (ESCA) provides a method complementary to ATR-IR for following transformations of PE-CO₂H. Table I shows the relative intensities of elements detected in PE-CO₂H and several derivatives and in model surfaces based on monolayer films. Three features of these data are relevant to chemistry of PE-CO₂H. First, PE-H itself shows ~5-10% of the oxygen-containing functionality present in PE-CO₂H. This functionality is probably hydroxyl and peroxy groups; no carbonyl absorption is visible in the ATR-IR. Thus, essentially all of the oxygen present as CO₂H groups in PE-CO₂H

Table I. Surface Concentrations of Selected Elements for Surface Functionalized Derivatives of Polyethylene and for Related Materials Determined by ESCA.

Material (Method) ^d	Surface Concentration (Atom %) ^{a,b,c}						
	C	O	N	S	P	Cl	Cr
PE-H ^e	99.4	0.6	<0.1	<0.1			<0.1
PE-H (PCl ₅ ; NH ₄ OH)	99.4	0.5	0.1				
PE-CO ₂ H	88.9	11.2	<0.1	<0.1			<0.1
PE-CO ₂ CH ₃ (H ⁺ , CH ₃ OH)	85.8	13.6	0.3	0.2	0.0	0.1	
PE-CONH ₂ (PCl ₅ ; NH ₄ OH)	89.7	6.5	3.8				
PE-CONHCH ₂ CH ₂ SO ₃ ⁻ (PCl ₅ ; H-R ₆)	70.4	18.5	3.2	2.3			5.5
PE[CO ₂ CH ₃][L ₅]	76.1	14.1	4.0	1.2	0.9	0.2	
PE[CO ₂ H][L ₅ D]	79.0	13.7	4.7	1.2	1.2	0.2	
Glass[[CH ₂] ₁₅][CO ₂ CH ₃][L ₅ D]	70.1	17.9	3.6	0.8	0.1	0.2	7.4
Si/SiO ₂ [[CH ₂] ₁₅][CO ₂ CH ₃][L ₅ D]	62.0	20.1	5.0	2.0	0.2	0.0	10.6
Au[Dansyl Cystine]	46.9	14.8	3.9	5.0	0.0	0.3	28.8
Au[HS(CH ₂) ₁₀ CH ₃]	61.7	0.1		2.3			35.9

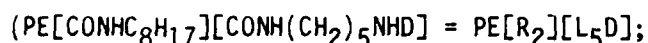
Table I (Notes)

- a A blank in this Table indicates that the element was not analyzed. We estimate uncertainties in these numbers to be $\pm 0.3\%$.
- b Sensitivity factors used were: C, 0.25; O, 0.66; N, 0.42; P, 0.39; Cl, 0.73; S, 0.54; Cr, 2.3; Na, 2.3; Si, 0.27; Au, 2.8.
- c Values listed as <0.1 are the result of analysis of the noise level present in the regions of interest. The original spectra of representative spectra of these regions have been published previously.
- d See Table II for definitions of L_5 and R_6 , and Scheme II for the preparation of the glass, silica, and gold-supported films.
- e Commercial (Flex-O-Glass Inc.) film was extracted for 18 h with refluxing CH_2Cl_2 before spectroscopic examination or chemical modification to remove additives (antioxidants, slip agents, and others).

is introduced on oxidation. Treatment of unoxidized PE-H with PCl_5 followed by NH_4OH introduces no oxygen or nitrogen. Second, inspection of the data in Table I indicates that this technique is only semiquantitative (at least, as we have conducted these experiments). Even in instances in which two elements not present in PE- CO_2H (or PE- COCl) are introduced in a known ratio, the analyzed relative surface concentrations (in atom %) are only approximately those expected. Thus, for example, the ratio of nitrogen to sulfur in PE- $\text{CONHCH}_2\text{CH}_2\text{SO}_3^-$ is 1.4 rather than 1.0. The origin of these and other similar disparities may be low signal-to-noise for low concentration elements, segregation of different elements in the surface and subsurface regions of the film, inappropriate sensitivity factors, or impurities. We have not tried to disentangle the sources of error, nor have we relied on the ESCA data in other than a qualitative sense. Third, derivatives of PE- CO_2H prepared by conversion to PE- COCl with PCl_5 always show small but significant signals from phosphorus left in the film in some form. We have not identified this (these) phosphorus-containing residues, but we have demonstrated that this residual phosphorus does not significantly influence the fluorescence properties of these surfaces by substituting SOCl_2 for PCl_5 in the preparation of PE- COCl . Films made with SOCl_2 had fluorescence properties indistinguishable from those made with PCl_5 .

Derivatives of PE- CO_2H Containing the Dansyl Group: PE[R₁][L₁D]:
Nomenclature, Synthetic Methods; Characterization. The complexity of the mixture of surface functionalities on PE- CO_2H and its derivatives makes it difficult to name the different materials produced in this work. Even a description that listed all of the functional groups present in the interfacial region and that specified their relative proportions--information

that is not available for any of these materials--would still leave questions of spatial distribution and local structure unresolved. In this and following papers, we need to be able to refer to polymer surfaces which have been modified by covalent attachment of functional groups. We use a system of nomenclature that is descriptive rather than complete. The group connecting the Dansyl (D) moiety to the polyethylene is specified by the letter L, and other functional groups present on the surface, whether introduced intentionally or produced as a side reaction, by the letter R. The subscript i in L_i (i.e. $L_6D = NH(CH_2)_6NHD$) indicates the number of carbon atoms in the linking chain. We refer to these materials either in terms of the groups listed in Table II and Scheme I ($PE[R_j][L_iD]$) or by a nomenclature intended to emphasize the functional groups believed to be important

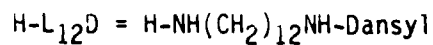
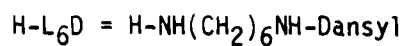
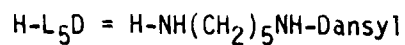
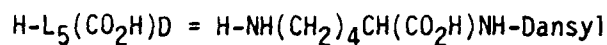
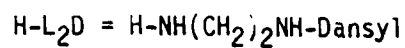


$PE[CONH(CH_2)_2SO_3^-][CO_2CH_3][CONH(CH_2)_2NHD] = PE[R_6][R_7][L_2D])$. Unless specified otherwise, this nomenclature assumes that the functional groups are ultimately connected to the polyethylene substrate through amide or ester groups. We emphasize that these descriptions are qualitative labels, and do not imply either complete description of the surface or adequate knowledge to offer a complete description. We refer generically to polyethylene having Dansyl groups covalently attached to its surface as PE-D.

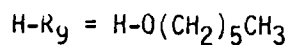
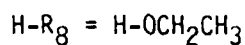
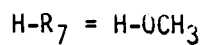
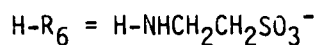
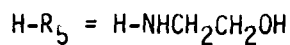
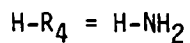
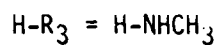
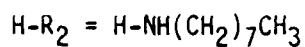
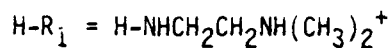
The fundamental procedure used to attach Dansyl groups to the surface of PE-CO₂H involves reaction of PE-COCl with a labeling reagent composed of a Dansyl group covalently linked to a reactive amine moiety (Scheme I). Perhaps because Dansyl groups are large and cannot pack at the same density as carboxylic acid groups, or perhaps simply as a result of competition between the Dansyl group and solvent as nucleophile, reaction of amino Dansyl derivatives with PE-COCl in methanol produces materials having both surface

Table II. Groups used to Modify the Surface of PE-CO₂H (Scheme I).
 D = Dansyl.

H-L_i-D



H-R_j



Dansyl and surface ester groups. The ATR-IR spectrum of the material prepared by reaction of PE-COCl with 1 in methanol is shown in Figure 1, together with assignments. There is no evidence for residual free hydroxyl groups or unreacted carboxylic acid moieties in the infrared spectrum of the product. Thus, all of the surface carboxylic acid moieties of PE-CO₂H have been consumed and converted either to Dansyl amides or to methyl esters. The ratio of S to O in PE[CO₂CH₃][L₅D] as measured by ESCA is 0.085; that for N to O is 0.28. These numbers suggest that approximately 25% of the carboxylate groups have been converted to derivatives of Dansyl (assuming a ratio of 3:2 for carboxylic acid and ketone groups on the surface³⁻⁵). This estimate is qualitatively compatible with the ratio of intensities of ester and amide peaks observed in the ATR-IR spectrum of this material (Figure 1).

The surface density of Dansyl groups in PE[CO₂CH₃][L₅D] (that is, the number of Dansyl groups per cm² of geometrical film area) was characterized by two procedures. In one, the Dansyl groups were removed from the surface by hydrolysis and the number released from a known geometrical area of polymer film measured in solution. From these measurements, we infer that 6×10^{14} Dansyl groups are present per cm² of geometrical film area. Comparison of this number with that determined earlier³ for the surface density of CO₂H groups indicates that ~30% of the carboxylic acid groups of PE-CO₂H are converted to Dansyl amides, and is again compatible with the estimates of conversion obtained from ATR-IR spectroscopy and ESCA of this material. Control experiments described in the experimental section established that the amino Dansyl compound 1 (H-L₅D; see below) does not react with unfunctionalized polyethylene (either with or without treatment with PCl₅), and that Dansyl groups covalently attached to polyethylene via amide moieties are not destroyed by the conditions used for hydrolysis in this assay

procedure. A second method of counting the surface-bound Dansyl groups involved total dissolution of the polymer. A sample (5 cm^2 of functionalized film) was dissolved in 5 mL of hexadecane at 100°C . The fluorescence intensity from this solution (at 100°C , $\lambda_{\text{max}} = 468 \text{ nm}$) was compared to that of solutions of 2 of known concentration in hexadecane at 100°C . The sample solution was found to have a similar intensity to a solution of 2 having a concentration of $1.1 \times 10^{-6} \text{ M}$. This comparison gives a value of $6.7 \times 10^{14} \text{ cm}^{-2}$ for the density of surface groups in $\text{PE}[\text{CO}_2\text{CH}_3][\text{L}_5\text{D}]$ and is in good agreement with the density inferred by hydrolysis.

The qualitative fluorescence behavior of $\text{PE}[\text{CO}_2\text{CH}_3][\text{L}_i\text{D}]$ on excitation at 350 nm shows several characteristic features. Dry film, or film wet with solvents, fluoresces visibly green. Fluorescence is quenched, as expected, on exposure of the film to 1.0 N HCl. The fluorescent properties of the film can be eliminated by rubbing the surface with a finger or a clean glass rod several times, operations that do not otherwise affect the appearance of the surface. The Dansyl groups of $\text{PE}[\text{CO}_2\text{CH}_3][\text{L}_i\text{D}]$ are not removed on extraction with solvent (24 h in refluxing CH_3OH).

Dansyl groups can be noncovalently introduced into unfunctionalized polyethylene or $\text{PE}-\text{CO}_2\text{H}$ by extended soaking in Dansyl-containing solutions: for example, treatment of PE with 10 mg of 1 dissolved in toluene (10 mL) for 1 h yields a film showing blue fluorescence. This fluorescence is not decreased by rubbing the surface or exposing it to aqueous acid. More than 90% of this adsorbed Dansyl is removed by extraction for 1 h in refluxing CH_3OH .

The procedure used to introduce other Dansyl derivatives onto the polyethylene surface is analogous to that described for $\text{PE}[\text{CO}_2\text{CH}_3][\text{L}_5\text{D}]$ (Scheme I). Most of these other derivatives were not characterized in the

same detail, but since the reactivity of the amino Dansyl derivative should be similar to that for 1 , we would expect roughly similar degrees of functionalization. In any event, our principal objective was to attach Dansyl groups covalently to the polyethylene surface, and within certain limits, the number density of attached Dansyl groups was relatively unimportant. Uncertainties concerning the absolute number of Dansyl groups attached to the polymer film do, however, make comparisons of absolute fluorescence intensities difficult, and certain of the comparisons of intensities made in the sections describing the fluorescence of these films should be considered to be approximate.

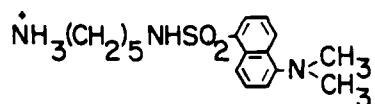
In certain experiments, we wished to modify the environment on the surface surrounding the Dansyl groups by introducing more or less polar functionalities. The simplest way to accomplish this objective was to treat PE-COCl with Dansyl derivatives in acetone, rather than methanol, and complete the reaction by rinsing the sample with water. The resulting material, PE[CO₂H][L₅D], has carboxylic acid groups on its surface (presumably derived by hydrolysis of unreacted acid chloride moieties). ATR-IR, ESCA and fluorescence intensity comparisons for PE[CO₂H][L₅D] indicate ~30% conversion of carboxylic acid groups present in PE-CO₂H to Dansyl derivatives, as was found for PE[CO₂CH₃][L₅D].

A second method for incorporating groups with differing polarities involved mixing the Dansyl-containing nucleophile (H-L₅D) with another compound of similar nucleophilicity (H-R_j) and allowing the two nucleophiles to compete for acid chloride groups on the surface (Scheme I). Detailed characterization of these surfaces would, in principle, be possible using isotopic labeling experiments, but would require a complex analysis. We have not characterized these surfaces to this extent. In general, we describe only

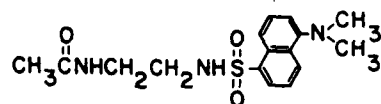
the ratio of reactive nucleophilic species present in the solution before reaction with PE-COCl, and assume that the distribution of functional groups covalently attached to the surface after reaction is approximately proportional to that present in solution before reaction.

A third method for making PE-D surfaces involved first making surfaces with free amino groups: PE-CH₂NH₂ (PE-CO₂H → PE-CONH₂ → PE-CH₂NH₂; Scheme I) and PE-CONHCH₂CH₂NH₂ (via PE-CO₂CH₃). These amine-functionalized surfaces were allowed to react with Dansyl chloride (shown in Scheme I for PE-CH₂NH₂).

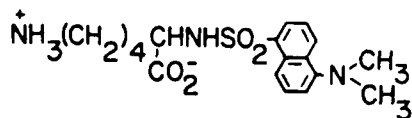
Model Systems: Soluble Derivatives of Dansyl. In order to be able to interpret the data obtained for PE-D surfaces we have studied the soluble Dansyl derivatives 1-3. Most of the work was carried out on 2; 1 and 3 were used only to verify that modifications in the connecting link L do not significantly influence the fluorescence of the Dansyl moiety.



1



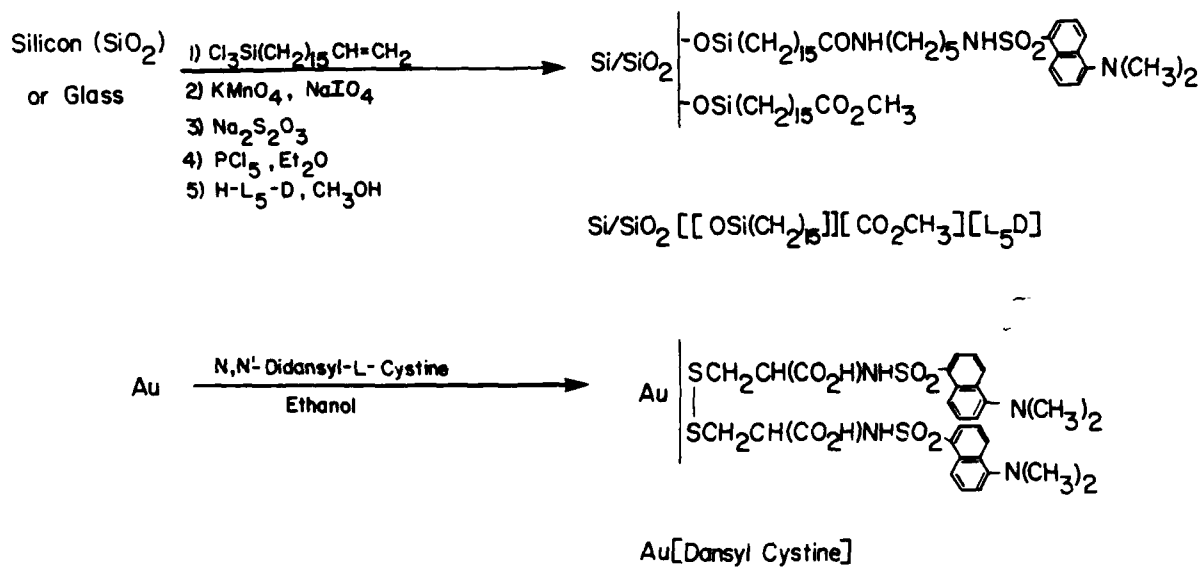
2



3

Model Systems: Functionalized Organic Monolayer Films. Because our knowledge of the density and three-dimensional distribution of Dansyl groups at the surface of PE-CO₂H is limited, we have prepared several model systems containing Dansyl groups attached to oriented organic monolayer films (Scheme II). Organic monolayers have been the object of extensive research in our laboratory, and details of the preparation and characterization of systems of the types used here will be described in separate papers. Here we only use them for comparison with PE-D, and we assert without proof that each is, in fact, a monolayer. Similar systems have been prepared and characterized by others.¹⁷⁻²³ The first group of these models are based on planar glass and silica (i.e. oxidized silicon) substrates functionalized using organosilane coupling agents.¹⁷⁻¹⁹ The second is based on thin evaporated gold films functionalized by spontaneous adsorption of previously functionalized organic disulfides.²⁰⁻²³ The nomenclature used in naming these systems is derived from that employed with PE-CO₂H (Scheme I), with the addition of double brackets to indicate the common coupling agent used to connect the surface to the Dansyl and carboxylic ester surface functionality.

The first system (based on glass or silica) was prepared by the following sequence of manipulations. A glass microscope slide or silicon wafer was cleaned and treated with an alkyltrichlorosilane having a terminal olefin group (here, Cl₃Si(CH₂)₁₅CH=CH₂). The terminal olefin group was oxidized to a carboxylic acid group by treatment with aqueous permanganate/periodate solution. The resulting carboxylic acid moieties were then coupled to Dansyl moieties using reactions closely analogous to those employed with PE-CO₂H. We refer to the resulting material as Glass[[OSi(CH₂)₁₅]][CO₂CH₃][L₅D]. The double bracket indicates that the glass surface is entirely functionalized



Scheme II. Organic Monolayer Films Used to Provide Models for PE-D.

with $-\text{OSi}(\text{CH}_2)_{15}-$ moieties. We indicate only one bond between oxygen and silicon. Others are undoubtedly present, but whether these surfaces contain high proportions of SiOSi bridges or other groups bonded to silicate groups in the glass remains unclear. The experiment protocol used to introduce the $[\text{OSi}(\text{CH}_2)_{15}]$ moiety in these experiments is based on widely used procedures for functionalization of organic surfaces with organosilanes;¹⁹ the oxidation of a terminal olefin to introduce a carboxylic acid group in this type of system is discussed by Sagiv.¹⁸ The second system involved the direct adsorption of commercially obtained Dansyl cystine onto gold surfaces.²⁰⁻²³ Here, we assume that the disulfide moiety is attached to the gold surface with the Dansyl group still attached.

Although fine details of the structures of all of these types of systems are still being explored, it is clear that all give approximately monolayer coverage of the starting inorganic support by the organic moieties; the two-dimensional density of carboxylic acid groups in the first system is $\sim 5 \times 10^{14} \text{ cm}^{-2}$. All of these systems are better defined structurally than $\text{PE-CO}_2\text{H}$ --even given current uncertainties concerning details of their structures--because the maximum depth of the organic interphase is limited by the extended length of the surface attached organic groups ($< 30 \text{ \AA}$). We propose these systems as model materials in which Dansyl groups are incorporated into authentic thin organic layers, and use them in interpreting the results obtained in studying the fluorescence of PE-D . We will not devote space in this paper to their further characterization, but studies directed to that end will be reported shortly.

Fluorescence of PE-D and Model Systems: Dependence on Solvent. Most of our work has been carried out with the Dansyl cadavarine derivatives of

PE-CO₂H, PE[CO₂H][CONH(CH₂)₅NHD] = PE[CO₂H][L₅D] and PE[CO₂CH₃][L₅D] (eq 1). Measurement of fluorescence spectra from these solid films required careful attention to detail to minimize scattering of the exciting radiation; the procedure used is sketched below and details are summarized in the Experimental Section. The technical problems in measuring these fluorescence spectra introduce a small but significant level of uncertainty concerning relative intensities. Because measuring the "concentrations" of Dansyl groups exposed to the exciting radiation is difficult in these heterogeneous systems, we have not attempted to measure absolute fluorescence intensities or quantum yields: all of the data given for intensity of fluorescence in a given heterogeneous system can be compared internally, but only qualitative comparisons with other heterogeneous systems are possible. Fluorescence intensities (I_f) given in this paper are the integrated areas of the observed fluorescence emission: they are not corrected for differences in instrumental sensitivity at different wavelengths. Swelling and buckling of the polymer film when in contact with nonpolar solvents (cyclohexane, toluene) may also lead to errors in measured intensities. Thus the fluorescence intensities for PE-D samples in these solvents should be considered estimates rather than precise values.

Fluorescence spectroscopy on Dansyl derivatives is, in general, straightforward. Dansyl is relatively insensitive to quenching by oxygen and trace impurities. The absorption maximum is essentially independent of medium: we used $\lambda_{\text{excitation}} = 350 \text{ nm}$ for all work. Fluorescence of the Dansyl group is destroyed on prolonged irradiation, but this phenomenon--irreversible photobleaching--posed little problem in this work because the extended exposures required to bleach PE-D significantly were long (hours) compared to the time required to make measurements (<2 minutes). The film

samples were positioned diagonally in the cell at an angle of $\sim 45-60^\circ$ relative to the exciting radiation in the cell. Reflection and scattering of the exciting radiation could be checked using samples differing in their preparation from those employed in the fluorescence studies only in the omission of the step leading to attachment of the Dansyl group. The solid supports used (polyethylene, glass, silicon) displayed, before attachment of Dansyl groups, little background fluorescence in the spectral range of interest.

Figure 2 and Table 3 summarize the observed fluorescence for $\text{PE}[\text{CO}_2\text{H}][\text{L}_5\text{D}]$ and 2 in a selection of solvents. The solvents used in these studies were among those selected by Dougherty and coworkers⁶ as part of their application of Dansyl derivatives to the study of macroreticular resins as fitting the multiparameter solvation energy relationship developed by Taft and Kamlet.²⁴ We have not used this relationship in the work described in this paper, and have instead referred to solvents in terms of dielectric constant (Figures 3 and 4). Nonetheless, the work of Dougherty *et al.* establishes that the behavior of the Dansyl fluorophore in these solvents is "well-behaved," and provides a series of carefully obtained data for comparison. We discuss each of these systems in turn.

The spectra of the soluble model compound 2 are those expected from previous work.^{6,7} As the solvent becomes more polar, λ_{max} shifts to longer wavelength (Figure 3), the intensity of fluorescence decreases (Figure 4), and the fluorescence peak width at half height increases.

Three features of the fluorescence spectra of $\text{PE}[\text{CO}_2\text{H}][\text{L}_5\text{D}]$ are significant. First, with the exception of the spectrum in $\underline{\text{c}}\text{-C}_6\text{H}_{12}$, all of the spectra have similar shape, width, and values of λ_{max} . The spectrum in $\underline{\text{c}}\text{-C}_6\text{H}_{12}$ has a shape suggesting contributions from Dansyl groups in more than

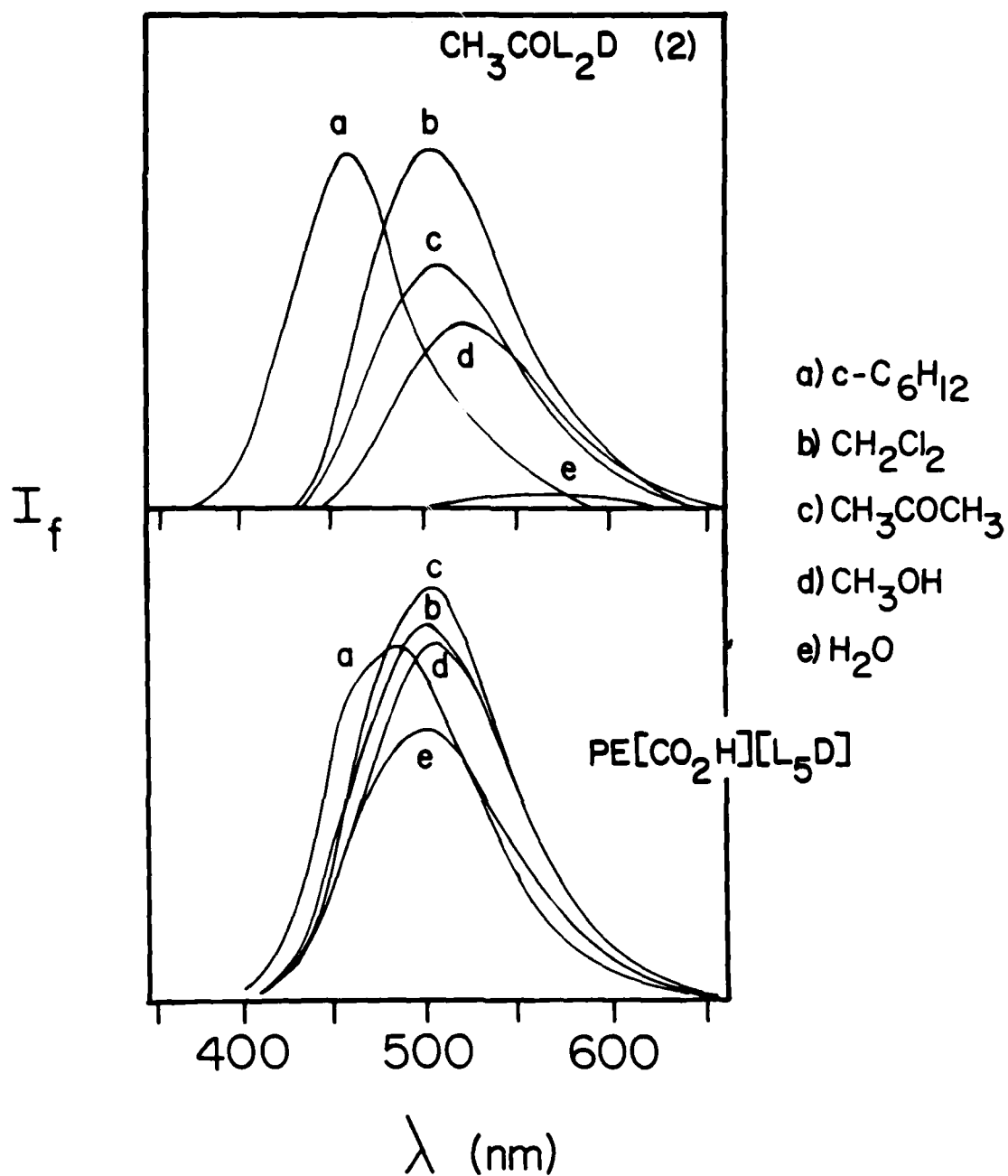


Figure 2. Fluorescence emission spectra of: upper, $\text{CH}_3\text{COL}_2\text{D}$ (2) in solution in representative solvents; lower, $\text{PE}[\text{CO}_2\text{H}][\text{L}_5\text{D}]$ in contact with the same solvents. For all samples the exciting frequency was 350 nm. Solution spectra were determined at 1.5×10^{-5} M.

Table III. Fluorescence of Dansyl Derivatives in Contact with Different Media.

Solvent	ϵ	CH ₃ COL ₂ D (2)			PE[CO ₂ H][L ₅ D]		
		λ_{\max} (nm)	$w_{1/2}$ (nm)	I_r^a	λ_{\max} (nm)	$w_{1/2}$ (nm)	I_r^a
cyclohexane	2.0	462	75	0.95	490	97	0.83
toluene	2.4	471	87	0.81	490	97	0.88
diethylether	4.3	479	90		490	96	0.85
methylene chloride	9.0	506	90	1.00	505	97	0.93
acetone	21	513	95	0.66	503	95	1.00
ethanol	24	516	95		502	97	0.93
methanol	33	525	105	0.49	508	100	0.87
dimethyl formamide	37				508	98	0.80
water	80	559	110	0.05	500	100	0.69

I_r^a is the relative intensity of fluorescence. Values for 2 are normalized with respect to that in methylene chloride; those for PE[CO₂H][L₅D] were normalized relative to the value in acetone. A blank indicates that the quantity was not measured.

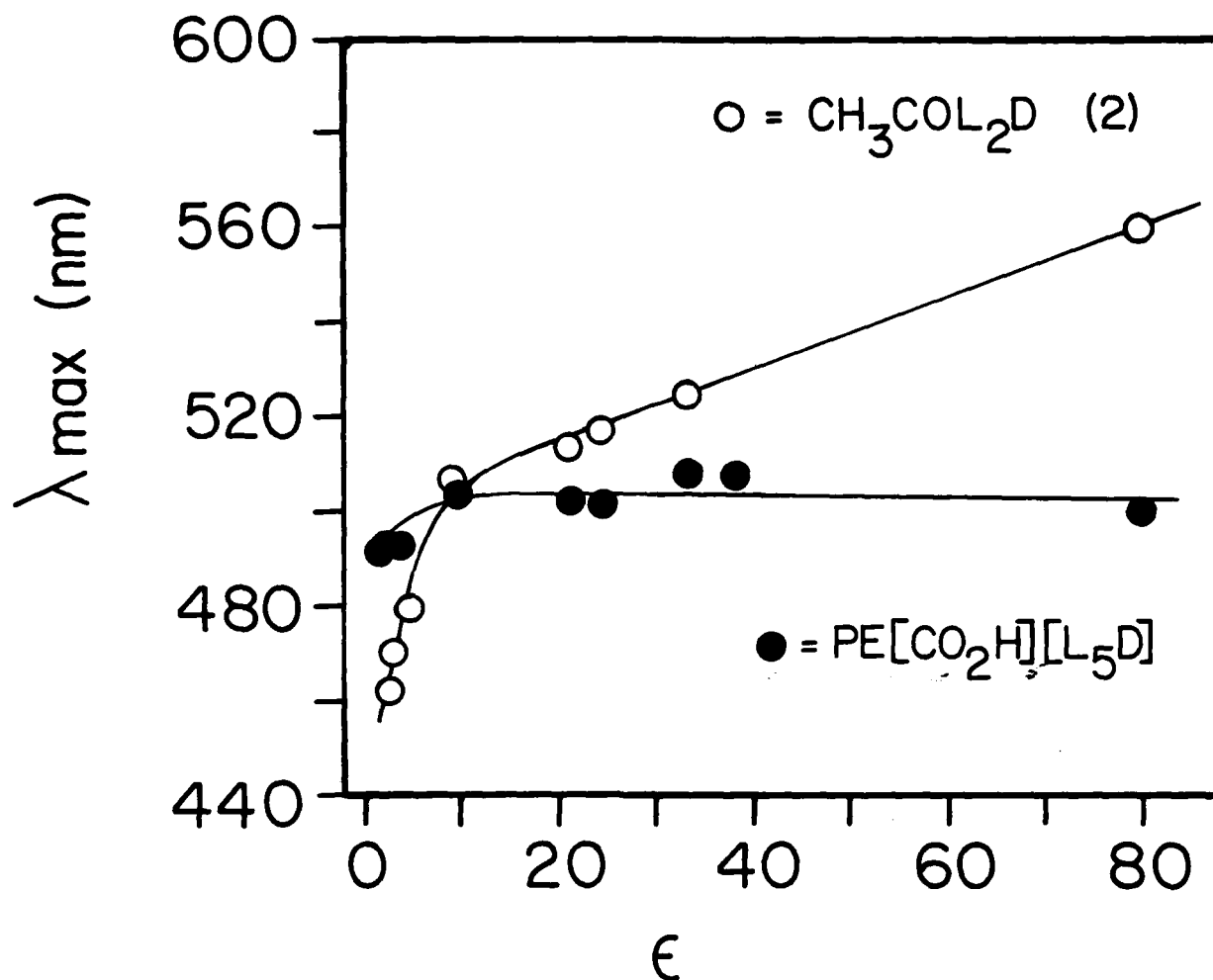


Figure 3. Fluorescence emission maxima for 2 (○) and $\text{PE}[\text{CO}_2\text{H}][\text{L}_5\text{Dansyl}]$ (●) as a function of solvent dielectric constant (data from Table III). The excitation wavelength for all samples was 350 nm. Solutions were 1.5×10^{-5} M (except cyclohexane, in which the probe was much less soluble). All soluble samples (except that in cyclonhexane) had adsorption = 0.061 ± 0.001 at 350 nm.

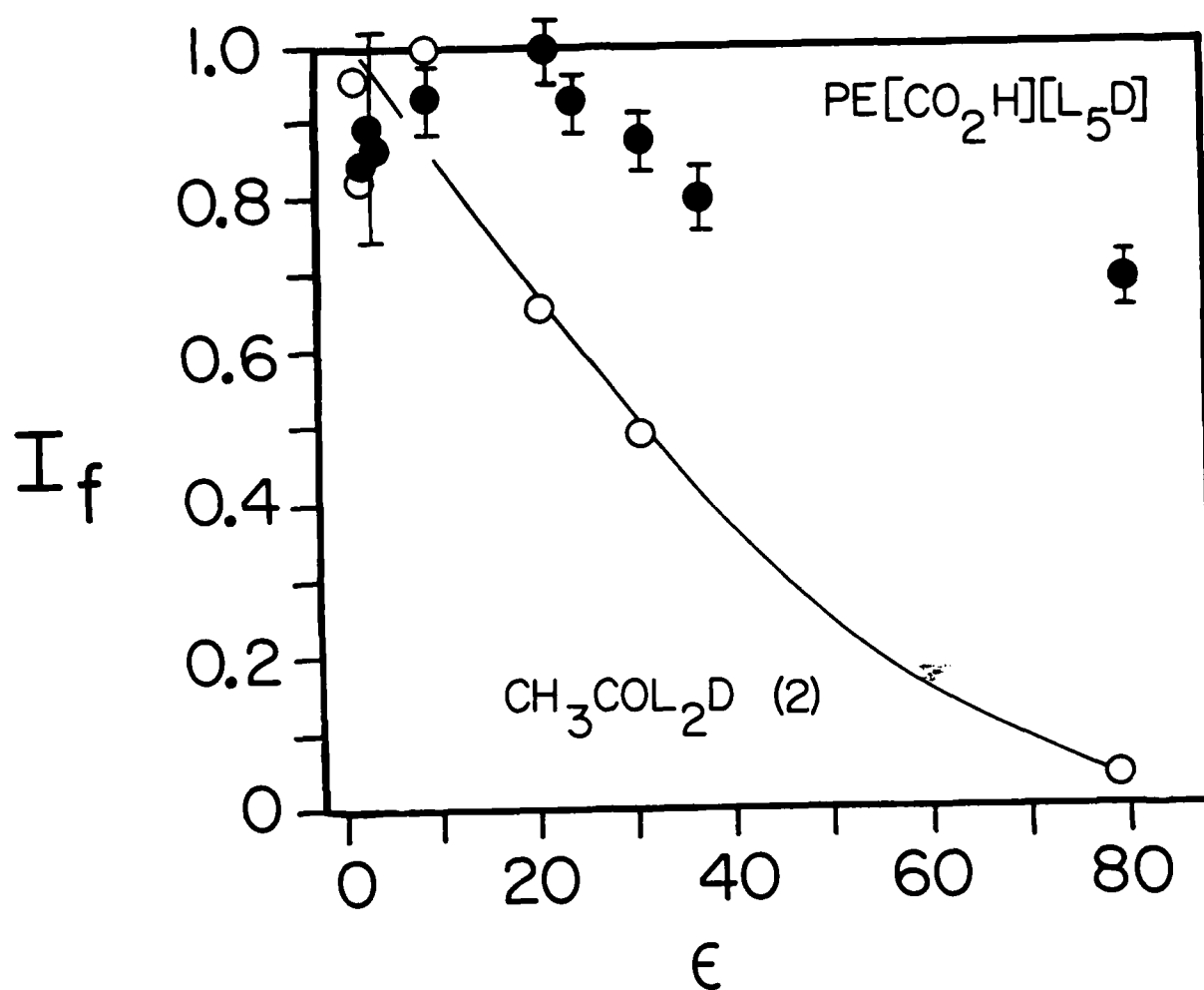


Figure 4. Fluorescence intensity (relative quantum yield, I_f) for 2 (○) and PE[CO₂H][L₅Dansyl] (●) as a function of solvent dielectric constant (data from Table III).

one environment (and the curve obtained in methanol hints at a shoulder at ~ 520 nm). Thus, the majority of the Dansyl groups contributing to the fluorescence seem to experience a uniform environment that is relatively insensitive to the polarity of the liquid in contact with the film. Second, the value of λ_{max} is only slightly dependent on the solvent in contact with the film (Figure 3); this value corresponds to that observed for $\underline{2}$ in solvents having intermediate polarity (i.e., CH_2Cl_2 , $\epsilon \approx 9$). Third, the dependence of the intensity of fluorescence on the liquid in contact with the polymer film is generally similar to (although smaller than) that observed with $\underline{2}$: the fluorescence from PE-D in contact with polar solvents (methanol, water) is less intense than that for PE-D in contact with with less polar solvents (Figure 4). Difficulties in measuring intensities accurately (especially for non-polar solvents, in which swelling and buckling of the film are important sources of error) prevent detailed liquid-to-liquid comparison. Roughly, however, the fluorescence intensity of this sample appears to decrease by approximately 20% on going from non-polar liquids to water. We believe but have not explicitly demonstrated that the values of I_f for $\underline{2}$ and PE-D surfaces in contact with various solvents are accurate indications of the relative fluorescence quantum yields in these solvents. Since both the absorbance at 350 nm (caption, Figure 3) and the number of Dansyl groups on the surfaces was unchanged on changing solvent then changes in fluorescence intensity should be determined by changes in the relative quantum yield.

We estimated semi-quantitatively the relative quantum yields for fluorescence of comparable soluble and polymer-bound systems in the following manner. We compared $\underline{2}$ in CH_2Cl_2 solution with $\text{PE}[\text{CO}_2\text{CH}_3][\text{L}_5\text{D}]$ in contact with water, these systems chosen because both give fluorescence at approximately the same wavelength. The excitation beam at our usual settings passes through

$\sim 0.36 \text{ cm}^3$ of liquid volume and strikes $\sim 0.51 \text{ cm}^2$ of the surface of a polymer film sample (placed in a cuvette) diagonally. At a surface density of 6×10^{14} Dansyl groups per cm^2 of polymer, this geometry places 5.1×10^{-10} mol of Dansyl groups in the path of the excitation beam. We observed that a solution of $\underline{2}$ in CH_2Cl_2 having a concentration of $1.4 \times 10^{-6} \text{ M}$ gives the same fluorescence intensity as $\text{PE}[\text{CO}_2\text{CH}_3][\text{L}_5\text{D}]$ in contact with water. At this concentration, approximately 5.1×10^{-10} mol of $\underline{2}$ is in the path of the excitation beam. Thus, we conclude that the quantum yield for fluorescence of the Dansyl groups of $\underline{2}$ in CH_2Cl_2 solution and of $\text{PE}[\text{CO}_2\text{CH}_3][\text{L}_5\text{D}]$ in contact with water are similar ($\pm \sim 10\%$).

The most striking features of the fluorescence spectra of PE-D are the insensitivity of these Dansyl groups (relative to structurally analogous Dansyl groups in solution) to changes in solvent character, and the suggestion (from peak shapes) that the dominant part of the fluorescence occurs from Dansyl groups occupying similar environments.

We suggest two interpretations of the data (the two being indistinguishable on the basis of the presently available data). The first is that all of the Dansyl groups in $\text{PE}[\text{CO}_2\text{H}][\text{L}_5\text{D}]$ are present in a uniform, relatively liquid-sensitive environment. In this interpretation, the shoulder observed at short wavelength (Figure 2) would reflect some undefined change in the film, perhaps reflecting its swelling in the non-polar solvents. The second interpretation is that the majority of the Dansyl groups occupy a common environment relatively uninfluenced by contacting liquid, but that a minority of them (perhaps $\sim 20\%$) are sensitive to the contacting liquid, and have fluorescence behavior similar to that of the soluble $\underline{2}$. This minority would appear as the shoulder at $\sim 460 \text{ nm}$ for the spectrum in $\underline{\text{c}}\text{-C}_6\text{H}_{12}$ and the hint of a shoulder at $\sim 520 \text{ nm}$ in methanol; no shoulder for these Dansyl

moieties would be visible in water, since fluorescence (at least for 2) is very weak in this medium (Figure 4).

Dansyl Attached to Monolayers. The fluorescence emitted by PE-Dansyl demonstrates that the major part of the functionalized interphase is relatively non-polar (similar to CH_2Cl_2 ; $\epsilon \sim 9$). In order to explore whether the region being sampled was near the surface rather than deeply buried in the polyethylene, the Dansyl moiety was attached to several monolayer systems of defined thickness. These systems, shown schematically in Scheme II, are only $\sim 25 \text{ \AA}$ thick, and should thus not have regions of deeply buried functionality. All Dansyl groups present will be at the "surface" (that is, at worst the Dansyl groups could be distributed over the outermost $\sim 25 \text{ \AA}$ of the sample; at best, they would be the outermost groups). Only the systems based on glass gave high fluorescence intensities, and even for these comparison of lineshapes with PE-D was rendered difficult by background scattering and fluorescence. Nonetheless the data in Table IV (obtained using water, ethanol and cyclohexane as the contacting liquids) indicate that the values of λ_{max} for these monolayers are essentially the same as for the Dansyl groups of PE-D. In addition, the values of $\text{pK}_{1/2}$ (the value of acidity of an aqueous solution in contact with these samples at which protonation by acid has reduced the fluorescence to half its original value) are very similar for PE-D and for the dansyl-containing monolayers (see below). The similarity of the data from these systems establishes that the fluorescence properties of the Dansyl groups of PE-D do not require that these groups be hundreds of Angstroms from the bulk water phase; the monolayer systems show the same behavior with a thickness of less than 30 \AA . Since the organic monolayers based on silane coupling agents may, however, be only weakly ordered (that is,

Table IV. Fluorescence properties of dansyl attached to various surfaces.

System/Substrate	Intensity ^a	λ_{max} (nm)		$w_{1/2}$ (nm)	$pK_{1/2}$ ^d
		<u>C</u> -C ₆ H ₁₂	H ₂ O (pH 4)		
PE[CO ₂ CH ₃][L ₅ D]	Very Strong	490	500	100	0.9
Glass[[OSi(CH ₂) ₁₅][CO ₂ CH ₃][L ₅ D]	Strong	492	505	102	1.2
Si/SiO ₂ [[OSi(CH ₂) ₁₅][CO ₂ CH ₃][L ₅ D]	Weak	<u>C</u>	<u>C</u>	100	<u>C</u>
Au[Dansyl Cystine]	None	<u>C</u>	<u>C</u>	<u>C</u>	<u>C</u>

^a In contact with water.

^b The $pK_{1/2}$ is the value of pH for an aqueous solution in contact with the sample that reduces the fluorescence intensity to one-half its unquenched value.

^c The quantity could not be measured accurately due to low intensity of fluorescence.

more like liquids than crystalline solids), these data do not require the Dansyl groups of either system to be in direct contact with the liquid phase.

An interesting aspect of the fluorescence results summarized in Table IV is the difference in intensities of the samples. Fluorescence quenching occurs at semiconductor and conductor surfaces by energy transfer to the bulk.^{25,26} We suggest that this type of quenching explains the low fluorescence intensity for the silicon substrate and the lack of fluorescence for the gold samples. Other, geometrical, factors may also be relevant. Since the rough samples of PE-CO₂H used here have approximately four times the number of surface groups as does a planar close packed monolayer of the same geometrical area ($2 \times 10^{15} \text{ cm}^{-2}$ vs $5 \times 10^{14} \text{ cm}^{-2}$) the fluorescence is expected to be more intense in PE-D simply because it has more surface groups. Also since much of the PE surface is not carboxylic acids it is possible that packing of Dansyl groups on this surface can reach more CO₂H sites than on a monolayer surface where a Dansyl on one site may sterically block neighboring sites. The lack of fluorescence from Au[Dansyl cystine] and weak fluorescence from Si[[OSi(CH₂)₁₅][CO₂CH₃][L₅D] is not due simply to fewer groups on the surface. ESCA (Table I) indicates that the glass and silicon samples have roughly the same number of attached Dansyl groups based on the intensity of N and S signals relative to C, Si and O. ESCA also suggests that the coverage of Dansyl groups on Au[Dansyl cystine] is high. By comparison to the S signal obtained from HS-(CH₂)₁₀CH₃ monolayers adsorbed on gold (a system known to pack with very high density) we conclude that the Dansyl groups are also densely packed.

The primary conclusion from comparison of data for fluorescence of PE-D and Dansyl-containing monolayer films is that the majority of the Dansyl groups contributing to the fluorescence in each occupy similar environments.

The limited thickness ($<30 \text{ \AA}$) of the monolayer system establishes that the thickness of the functionalized interphase of PE-D need be no greater than this value; it does not, however, set this value as an upper limit.

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Fluorescence Depolarization of 2 and PE[CO<sub>2</sub>CH<sub>2</sub>]CL-D<sub>1</sub>: Evidence for  
Energy Transfer in Polymer-Bound Dansyl. It is possible to establish that the  
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 Dansyl groups of PE-D are sufficiently close together for energy transfer to occur, by examining fluorescence depolarization.²⁷ The fluorescence lifetime of dilute Dansyl in solution is 14 ns.⁹ A freely rotating Dansyl group (e.g. 2 in a low-viscosity solvent) would be expected to lose all memory of the sense of polarized excitation before fluorescence emission; a Dansyl group prevented from rotating freely should emit polarized light with some degree of correlation between the plane of polarized excitation and the plane of polarized emission. We determined the polarization P (eq 2, where V_H and L_H are the intensities observed for vertically and horizontally polarized emission when the excitation is polarized horizontally, and V_V and L_V are respectively the intensities of the vertical and horizontal emission when the excitation is polarized vertically) of fluorescence from 2 dissolved in, and

$$P = \frac{V_V - \frac{L_V V_H}{L_H}}{V_V + \frac{L_V V_H}{L_H}} \quad (2)$$

from $\text{PE}[\text{CO}_2\text{CH}_3][\text{L}_5\text{D}]$ in contact with, media of different viscosities (Figure 5). As expected, the degree of polarization of emission for $\tilde{2}$ increases with the viscosity of the medium, reaching a limiting value of ~ 0.33 (Chen reports a value of $P_0 = \sim 0.37$ for Dansylproline and Dansylglycine)²⁸ in high-viscosity solvents. The effective viscosity experienced by the Dansyl groups of $\text{PE}[\text{CO}_2\text{CH}_3][\text{L}_2\text{D}]$ would be expected to be high; the attachment of the Dansyl group to the solid polymer prohibits isotropic rotation entirely. The polarization of fluorescence of polymer-bound Dansyl groups is, however, relatively low (approximately that observed for $\tilde{2}$ in 85% glycerol in H_2O at 20 °C; $\eta \sim 100$ cp) and nearly independent of the viscosity of the contacting liquid. A similar depolarization is observed for solid $\tilde{2}$ (obtained from a powder in which the effective viscosity is very high.

We conclude from these experiments that the Dansyl groups attached to the polymer surface are sufficiently close together to allow energy transfer, and that the observed fluorescence depolarization reflects this energy transfer. Since such transfers can extend over tens of Ångströms this conclusion is physically plausible.²⁹ The observed density of surface Dansyl groups is $6 \times 10^{14} \text{ cm}^{-2} = 0.060 \text{ Å}^{-2}$. Even with a very liberal estimate of the surface roughness factor for $\text{PE-CO}_2\text{H}$ of 10--an estimate that allocates an average of 170 Å^2 to each Dansyl moiety--the average intermolecular separation between Dansyl moieties is only 13 Å , well within the distance required for energy transfer.

Variations in the Structure of the Group L Linking the Dansyl Moiety to the Polymer Surface. The studies of the influence of the polarity of the contacting fluid medium on the fluorescence (the virtual independence of the position of the emission maximum on the dielectric constant of the contacting

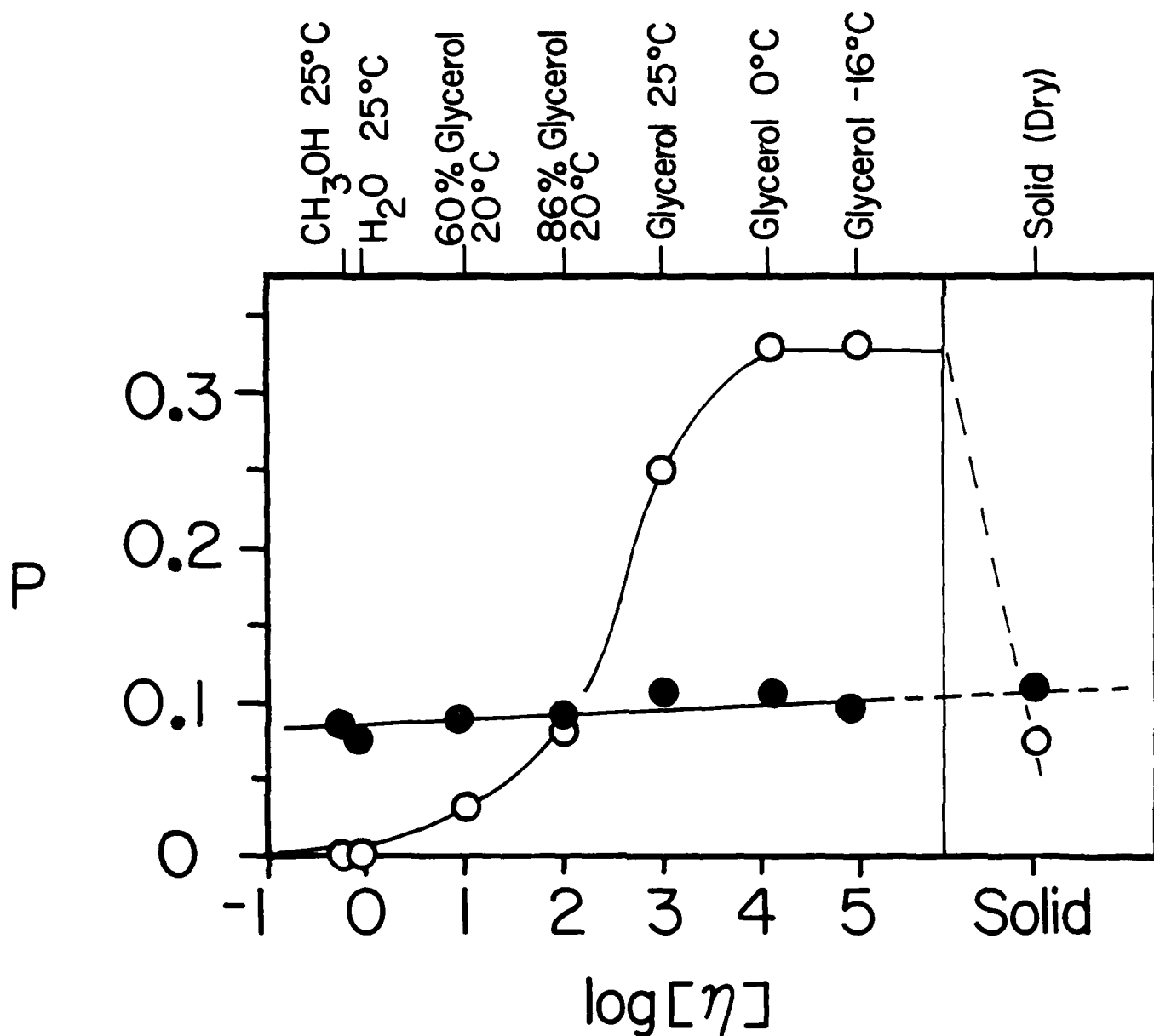


Figure 5. Fluorescence polarization P (eq 2) of 2 (○) and $\text{PE}[\text{CO}_2\text{CH}_3][\text{L}_5\text{D}]$ (●) in solvents with various values of viscosity η at the temperatures indicated. The units of η are cp.

liquid medium and the low dielectric constant suggested by the position of this emission maximum) indicate that the environment sampled by the majority of the Dansyl moieties is relatively low in polarity and almost unaffected by the liquid. In order to give more detail to the structure of the interfacial layer, we have varied the structure of the interfacial layer by varying the structures both of the group L linking the Dansyl moiety to the surface and of the group R sharing on the surface with the Dansyl moiety. Changes in the length of the polymethylene chain connecting the polyethylene amide and Dansyl sulfonamide moieties had no significant effect on λ_{\max} (using water as the contacting liquid): for the groups in Scheme I, $\lambda_{\max}(L_2) = 500$ nm; $\lambda_{\max}(L_5) = 500$ nm; $\lambda_{\max}(L_6) = 500$ nm; $\lambda_{\max}(L_{12}) = 490$ nm. All indicate a similar low polarity. Results for the members of this series were also very similar in contact with methanol ($\lambda_{\max} = 505$ to 508) nm.

All of the components of these systems are strongly hydrophobic; acetyl derivatives of the higher members of this series (e.g. $\text{CH}_3\text{COL}_6\text{D}$) are, for example, virtually completely insoluble in aqueous solution at neutral pH. We therefore expected these films to be collapsed (or condensed) onto (or into) the underlying hydrophobic polymer when the system was in contact with water. In an effort to break up this non-polar interphase, we attached the Dansyl group to the surface using more polar linking groups L. In particular, α -Dansyl-L-lysine (3) was attached to the polymer surface by the ϵ -amino group of the lysyl moiety $\text{PE}[\text{CO}_2\text{H}][\text{L}_5(\text{CO}_2\text{H})\text{D}]$. This functionalized interphase incorporates an extra carboxylic acid moiety (from the lysine moiety) and is correspondingly more hydrophilic than $\text{PE}[\text{CO}_2\text{H}][\text{L}_5\text{D}]$. Moreover, by changing the pH to a basic value, it should be possible to deprotonate all the carboxylic acid groups of the surface, and thus render it even more hydrophilic. Results are summarized in Figure 6.

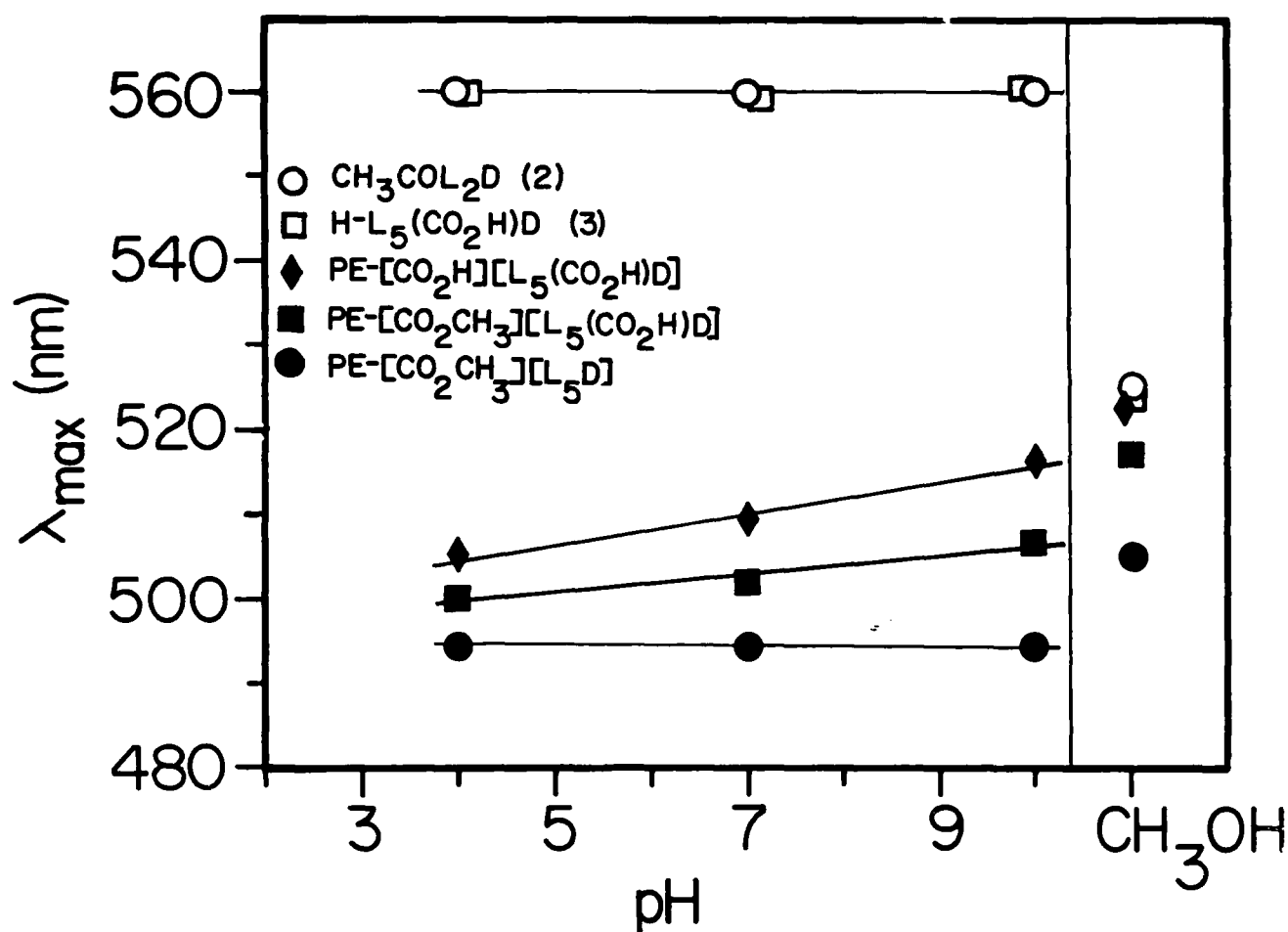


Figure 6. Emission maximum as a function of pH for several PE-D surfaces (with carboxylic acid groups in the linking group L, with carboxylic acid groups on the surface and in L, and with no carboxylic acid groups) and for the soluble models 2 and 3. The emission maxima in methanol are also shown for comparison.

There is essentially no difference in fluorescence between the two soluble Dansyl derivatives examined (2 and 3): introduction of the carboxylic acid group close to the Dansyl moiety has no influence on its fluorescence. There is also no pH dependence on the value of λ_{\max} for 3: conversion of the free carboxylic acid group of this substance to a carboxylate ion does not influence the fluorescence of the Dansyl group.

The values of λ_{\max} observed for the $\text{PE}[\text{CO}_2\text{H}][\text{L}_5(\text{CO}_2\text{H})\text{D}]$ do suggest a more polar environment for the Dansyl groups than that inferred for systems such as $\text{PE}[\text{CO}_2\text{CH}_3][\text{L}_5\text{D}]$ that have non-polar linking groups. Figure 6 shows a plot of λ_{\max} for two of these surfaces as a function of pH. Also shown is $\text{PE}[\text{CO}_2\text{CH}_3][\text{L}_5\text{D}]$ for comparison. At low pH these surfaces are more polar (experience a higher ϵ , probably due to increased swelling by water) than $\text{PE}[\text{CO}_2\text{CH}_3][\text{L}_5\text{D}]$ as would be expected. As the pH is increased, we expect the carboxylic acid groups, both those in the $\text{L}_5(\text{CO}_2\text{H})\text{D}$ moiety and those remaining unutilized on the surface, to ionize. This ionization and increase in local polarity would increase λ_{\max} . Not surprisingly, even at high pH these interphases retain a dielectric constant significantly lower than bulk water: at pH 10 $\text{PE}[\text{CO}_2^-][\text{L}_5(\text{CO}_2^-)\text{D}]$ has $\lambda_{\max} = 516 \text{ nm}$, a value similar to that for 2 in ethanol. This value suggests an increase in ϵ from ~ 9 at pH 4 ($\lambda_{\max} = 506 \text{ nm}$) to ~ 24 at pH 10. While these numbers are not highly accurate, they do give a qualitative idea of the magnitude of change in polarity at the interphase. We conclude that the low dielectric constants observed are not solely the result of the preference of the hydrophobic Dansyl groups for underlying bulk polyethylene compared to water (the charged $\text{L}_5(\text{CO}_2^-)\text{D}$ moiety would certainly dissolve more readily in water than in polyethylene), and probably reflect the intrinsic polarity of the

functionalized interphase with its mixture of Dansyl groups, amide and ester (acid moieties), methylene units, and permeating solvent molecules.

Variations in the Structure of the Group R in PE[R][L₅D]. As a second approach to changing the polarity of the interphase incorporating the Dansyl moiety, we varied the structure of the group R_j (Table II). Preparation of these materials involved reaction of a mixture of NH₂(CH₂)₅NHD and an appropriate nucleophile, H-R_j, with PE-COCl, typically in CH₃OH. We have not established quantitatively the relative density of -CONH(CH₂)₅NHD, -COR_j, and -CO₂CH₃ moieties on the polyethylene surface. The significant decrease in the intensity of fluorescence of these surfaces compared to those made without H-R_j moieties indicates clearly, however, that a significant population of -COR_j groups are introduced by this procedure. As with variations in the group L_i, the range of values of λ_{max} observed on varying R_j is relatively small (Table V). The most polar of these surfaces (PE[CONH(CH₂)₂OH][L₅D], λ_{max} = 511 nm) seems less polar than PE[CO₂⁻][CONH(CH₂)₅CH(CO₂⁻)NHD] (λ_{max} = 516 nm). The surfaces incorporating large saturated organic groups (e.g. PE[CONH(CH₂)₇CH₃][L₅D]) (λ_{max} = 470-490) do, however, seem to be significantly less polar than other surfaces we have examined.

The effect on λ_{max} of varying the R group can also be seen as a function of pH. The presence of ionizable groups leads to changes in the local polarity and is reflected in λ_{max}. Figure 7 shows this effect for basic and acid groups, with PE[CO₂CH₃][L₅D] for comparison. The presence of acidic species leads to an increase in λ_{max} with increasing pH as the groups ionize, leading to greater swelling. By contrast, the incorporation of basic groups leads to a decrease in λ_{max} with increasing pH as the amino group is deprotonated. We conclude that the nature of the surface groups on PE-D

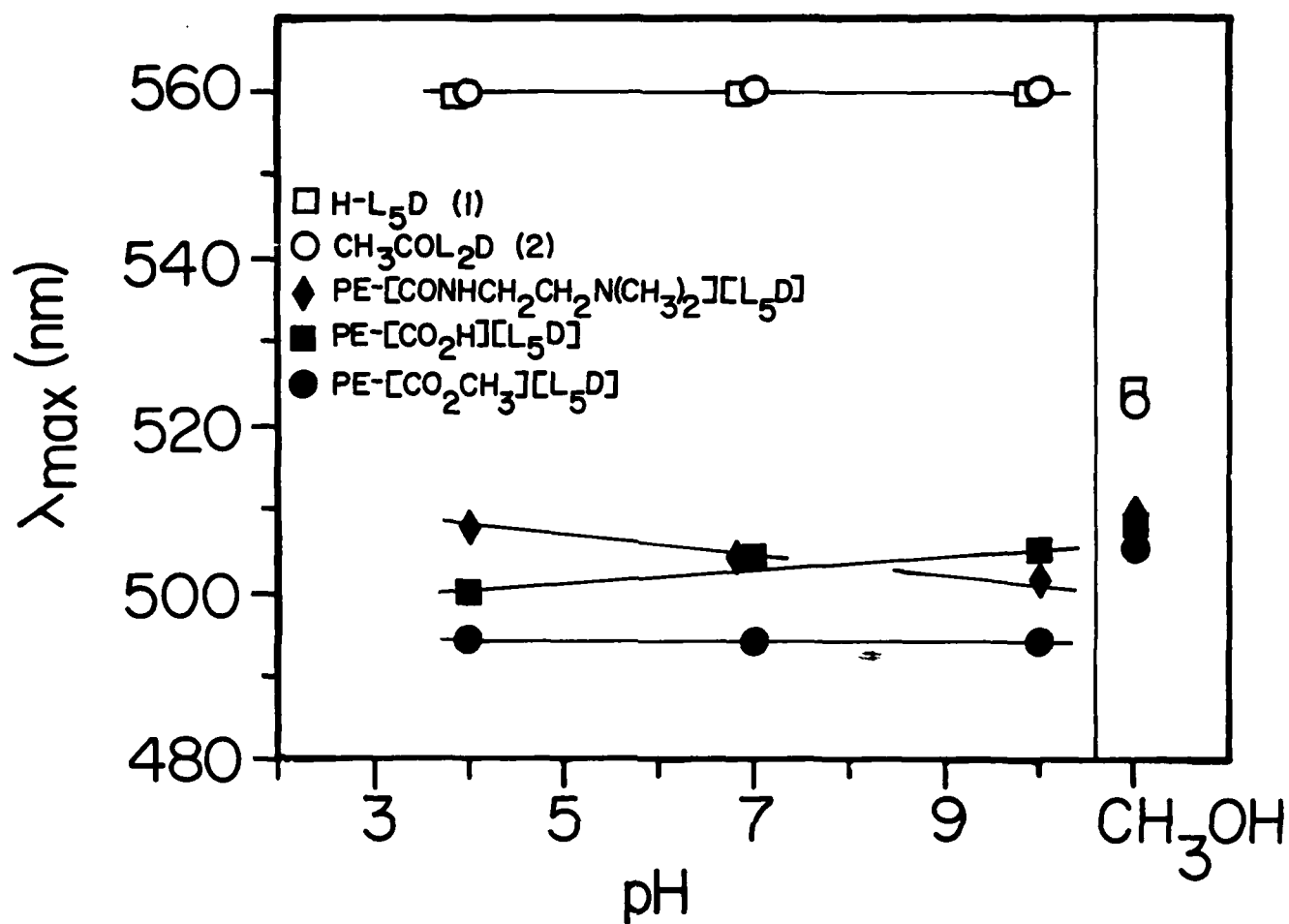
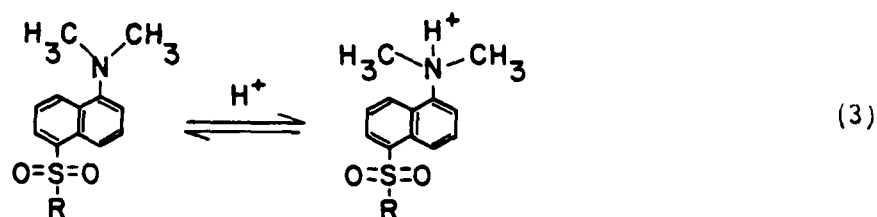


Figure 7. Emission maximum as a function of pH for PE-D surfaces with acidic, basic and neutral surface species and for the soluble models 1 and 2. The emission maxima in methanol are also shown for comparison.

surfaces influences the local polarity of the interphase, but that the extent of this influence is relatively small.

Quenching of Fluorescence of Surface-Immobilized Dansyl Groups by Protonation. A useful characteristic of the Dansyl group is that its fluorescence is quenched in acidic media (eq 3).³⁰ The characteristic



quenching of the fluorescence of Dansyl in media sufficiently acidic to protonate the dimethylamino group provides another probe that can be used to explore the interphase of the Dansyl-functionalized polyethylene. Increasing the acidity of the medium results in an increase in the extent of protonation and in a corresponding decrease in the intensity of fluorescence. We use the value of the solution pH required to reduce the fluorescence intensity to one-half of the value of unprotonated Dansyl as an empirical measure of the effective basicity of the dimethylamino group, and we call this value $\text{pK}_{1/2}$. We have examined the pH dependence of the intensity of fluorescence of a number of materials having composition $\text{PE}[\text{R}_j][\text{L}_5\text{D}]$ and of soluble and insoluble models for the Dansyl moiety in these materials. Figure 8 shows representative curves and Table V gives more extensive listings of values of $\text{pK}_{1/2}$.

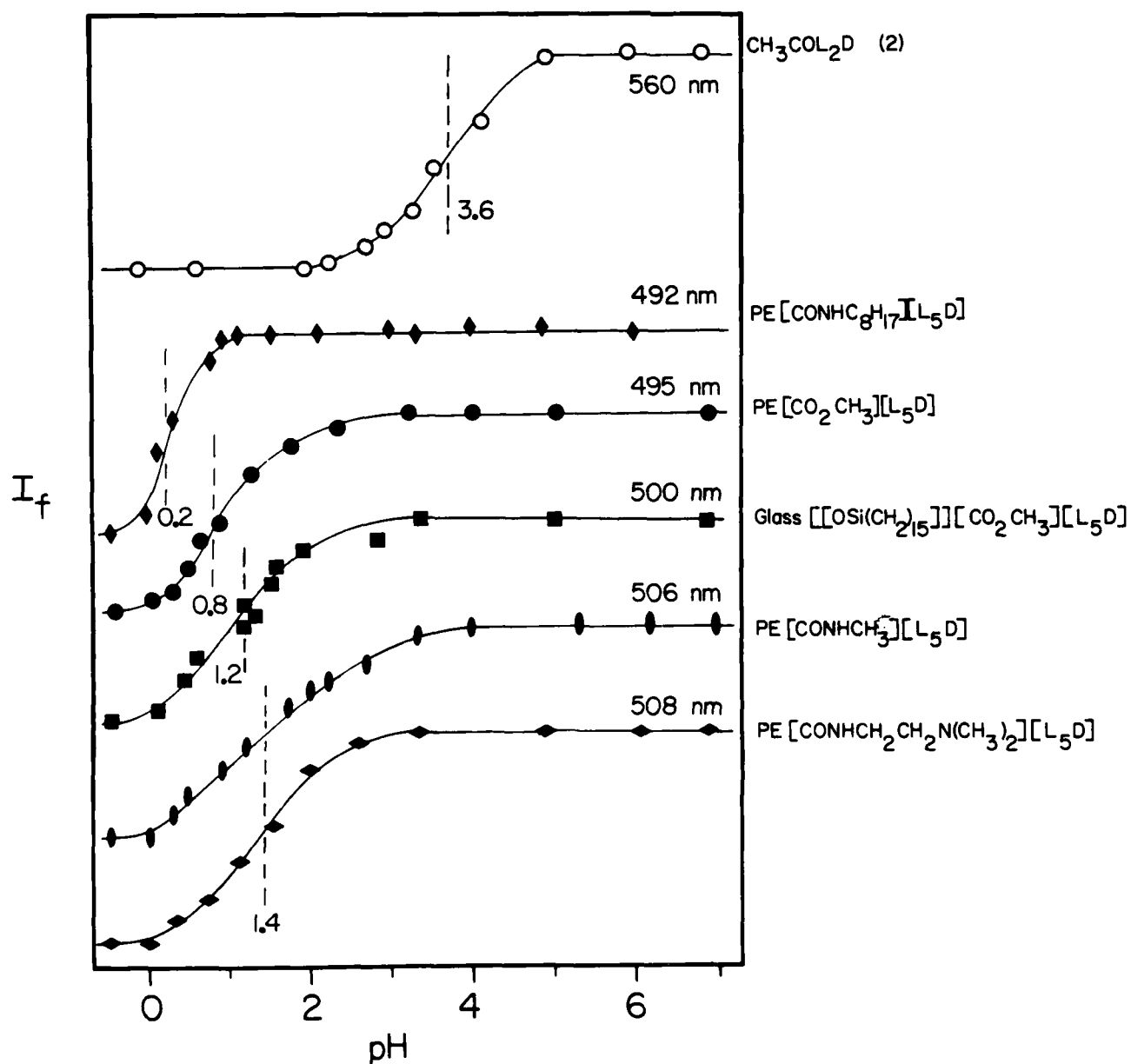


Figure 8. Fluorescence intensity as a function of solution pH for several PE-D samples. Also shown is 2 in water (1.5×10^{-5} M). The values of solution pH required to reduce the fluorescence intensity by one-half (the $\text{pK}_{1/2}$) are indicated by dashed lines. The emission maximum for each surface at pH = 4 is given on the right-hand side of each curve.

Table V. Fluorescence of Derivatives of Polyethylene, PE[COR_i][COL_jD], Monolayers and Soluble Dansyl Derivatives.

Sample	R/L Molar Ratio ^a	$\text{pK}_{1/2}$ ^b	λ_{max} (nm, pH 4)
<u>Soluble Analogues</u>			
$\text{CH}_3\text{COL}_2\text{D}$ (2)		3.6	560
H- $\text{L}_5(\text{CO}_2\text{H})\text{D}$ (3)		*	560
H- L_5D (1)		3.5	560
<u>Polyethylene Derivatives</u>			
1) PE[CONH(CH ₂) ₇ CH ₃][L_5D]	0.8	0.2	492
2)	8.0	<0	470-490 ^c
3) PE[CO ₂ (CH ₂) ₅ CH ₃][L_5D]	<u>d</u>	0.5	493
4) PE[CO ₂ CH ₂ CH ₃][L_5D]	<u>d</u>	0.5	495
5) PE[CO ₂ CH ₃][L_5D]	<u>d</u>	0.8	495
6) PE[CO ₂ [H ₃][L_2D]	<u>d</u>	0.95	500
7) PE[CONHCH ₂ CH ₂ N(CH ₃) ₂][L_5D]	1.0	1.5	508
8)	7.6	1.4	508
9)	38	1.3	508
10) PE-NH ₂ D		1.35	500
11) PE-CONHCH ₂ CH ₂ NHD		1.3	500
12) PE[CONHCH ₃][L_5D]	0.9	0.9	499
13)	8.6	1.4	506
14) PE[CO ₂ H][L_5D]	<u>d</u>	1.7	500
15) PE[CONH ₂][L_5D]	12	1.55	500
16) PE[CONHCH ₂ CH ₂ OH][L_5D]	0.55	0.8	497
17)	1.7	1.4	505
18)	2.7	2.3	511
19)	8.2	2.3	511
20) PE[CONHCH ₂ CH ₂ SO ₃ ⁻][L_5D]	3.4	3.7	507
21)	6.7	3.4	506
22)	34 ^e	5	506
23)	34 ^f	4.8	507
24)	189	~4.7	507

Table V (cont'd)

Monolayer Derivatives

25) Glass[[OSi(CH ₂) ₁₅]][CO ₂ CH ₃][L ₅ D]	<u>d</u>	1.2	500
26) Si/SiO ₂ [[OSi(CH ₂) ₁₅]][CO ₂ CH ₃][L ₅ D]	<u>d</u>	*	500

a A blank in this column means no H-R_j nucleophiles were added. This ratio is that in the reacting mixture and may be different than the ratio of species which become attached to the surface.

b An * in this column indicates the value was not determined.

c The peak for this surface was not sharply defined.

d Ester groups were introduced by conducting coupling reactions in the corresponding alcohol as solvent. Carboxylic acid moieties were introduced by hydrolysis of unreacted acid chloride moieties during or after reactions conducted in acetone.

e This surface was made using 10 mg of H-L₅D and 1 mL of 1 M taurine (see Experimental).

f This surface was made using 100 mg of H-L₅D and 1.25 g of taurine (see Experimental).

The soluble compound 2 shows a well-defined titration curve with $pK_{1/2} = 3.6$; this value is in good agreement with the literature value³⁰ for the pK_a of the dimethylamino group of Dansyl. Attaching the Dansyl group to polyethylene renders it more difficult to protonate. The titration curves shown for these derivatives of $PE[R_j][L_5D]$ are, in general, not simple sigmoidal curves. For example, in the case of $PE[CO_2CH_3][L_5D]$, the fluorescence titration curve covers only one pH unit centered at $pK_{1/2} = 0.8$. By contrast, the curve for $PE[CONH(CH_2)_2NH(CH_3)_2^+][L_5D]$ covers 3 pH units centered at $pK_{1/2} = 1.4$. The broad curve may represent the sum of overlapping curves with different values of $pK_{1/2}$; the fluorescence titration curves for $PE[CONH(CH_2)_2SO_3^-][L_5D]$ clearly show such overlap (Figure 9). The interface of this material apparently contains at least two distinct types of Dansyl groups: one at approximately $pK_{1/2} = 0.8$ (plausibly due to Dansyl groups adjacent to CO_2CH_3 moieties, these being generated during the functionalization of the surface) and another with $pK_{1/2} \approx 5$ (Dansyl groups adjacent to RSO_3^- moieties). By varying the concentration of $NH_2CO_2CH_2SO_3^-$ used in this preparation, we could prepare materials containing different ratios of Dansyl groups to sulfonic acid groups with the two characteristic values of $pK_{1/2}$. The fact that these values of $pK_{1/2}$ remain roughly invariant while their ratio changes, suggests that this rationalization for the form of the quenching curves for the several materials labeled $PE[CONH(CH_2)_2SO_3^-][CO_2CH_3][L_5D]$ is correct.

Similar experiments involving $H-R_5$ (ethanolamine) do not show this bimodal behavior (Figure 10). We cannot, in this instance, distinguish a single environment for the Dansyl moieties coupled with an unknown mechanism for broadening the fluorescence titration curve from a range of different

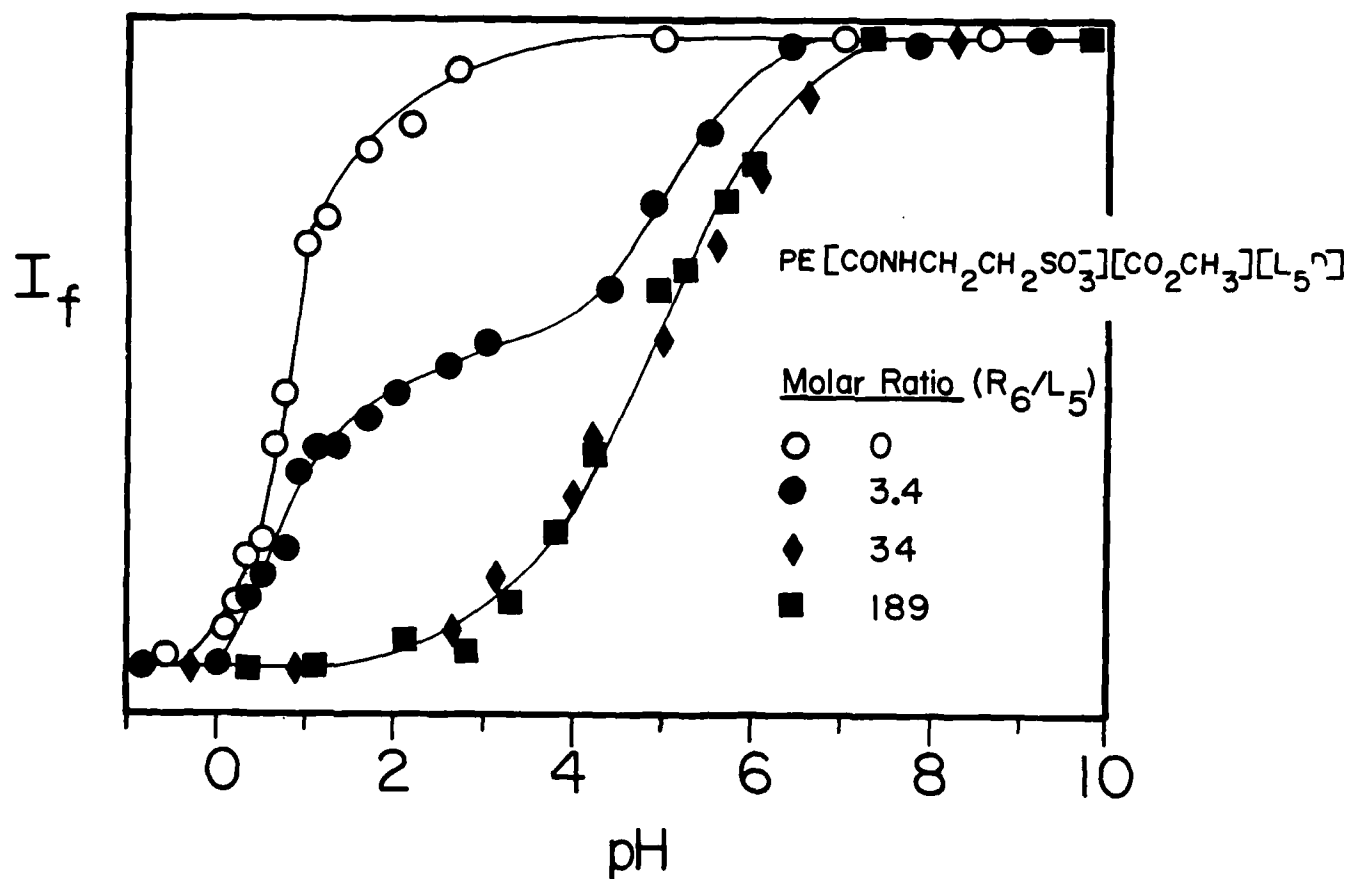


Figure 9. Fluorescence intensity as a function of pH for $\text{PE}[\text{CO}_2\text{CH}_3][\text{CONHCH}_2\text{CH}_2\text{SO}_3^-][\text{L}_5^+]$ with various ratios of taurine/Dansyl in the reaction mixture (\bigcirc , 0; \bullet , 3.4; \blacklozenge , 34; \blacksquare , 189).

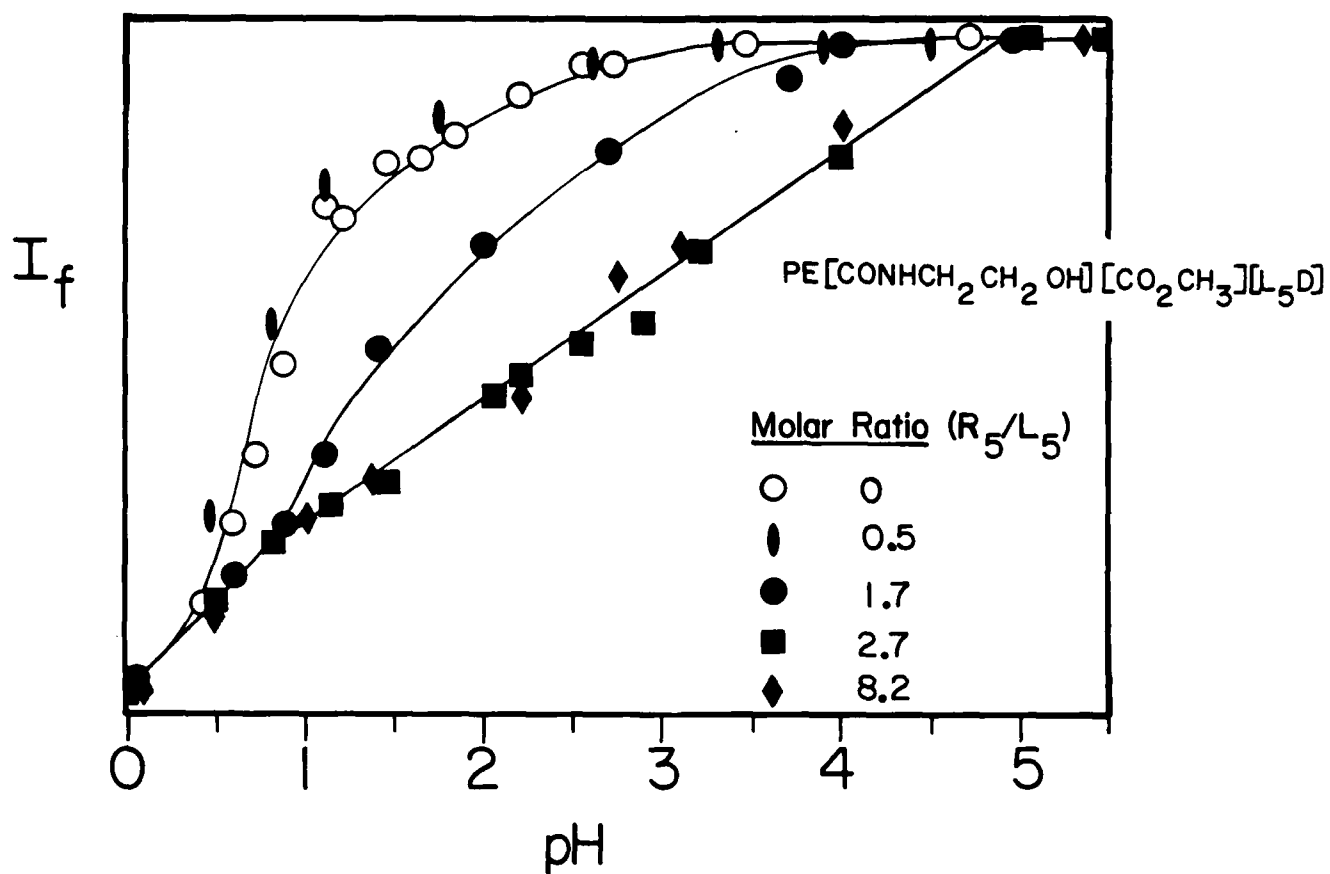


Figure 10. Fluorescence intensity as a function of pH for $PE[CONHCH_2CH_2OH][CO_2CH_3][L_5D]$ with various ratios of ethanolamine/Dansyl in the reaction mixture (○, 0; ◌, 0.5; ●, 1.7; ■, 2.7; ◆, 8.2). A surface was made with a molar ratio of 27 but the fluorescence was too weak to permit an accurate determination of the $pK_{1/2}$.

environments differing sufficiently little in their values of $pK_{1/2}$ as to be inseparable in the aggregate fluorescence titration curve.

Wetting of PE-D and Monolayer Analogs by Water as a Function of pH. The ionization of surface bound Dansyl moieties can be followed independently by measuring contact angles. We have shown previously that by varying the pH of aqueous drops used to measure contact angles, we could follow the ionization of surface bound carboxylic acid groups on PE-CO₂H: the more hydrophilic ionized CO₂⁻ species had, as expected, the lower contact angle.³ Figure 11 shows the advancing contact angle θ_a of buffered aqueous solutions on PE-[CO₂CH₃][L₅D] and PECH₂NH-Dansyl as a function of pH. The decrease in θ_a with decreasing pH correlates well with quenching of the Dansyl fluorescence. When the dimethylamino group is protonated the surface is more hydrophilic. The close correlation between θ_a and the fluorescence intensity is, however, surprising, since the values of $pK_{1/2}$ for Dansyl groups in the contact angle interphase (i.e. those groups close enough to the surface to influence wetting) might have been expected to be distinguishable from those deeper in the polymer. We attribute the decrease in θ_a at high pH to deprotonation of the sulfonamide group; we observe the same decrease for a surface containing sulfonamide groups but not Dansyl moieties (PE-CH₂NHSO₂CH₃).

The three monolayer-containing materials that incorporate Dansyl groups show titration curves similar to that of the analogous polyethylene-derived substances (Figure 12). The similar behavior of contact angle as a function of pH also provides evidence for the presence of Dansyl groups on the silicon and gold surfaces which show little or no fluorescence.

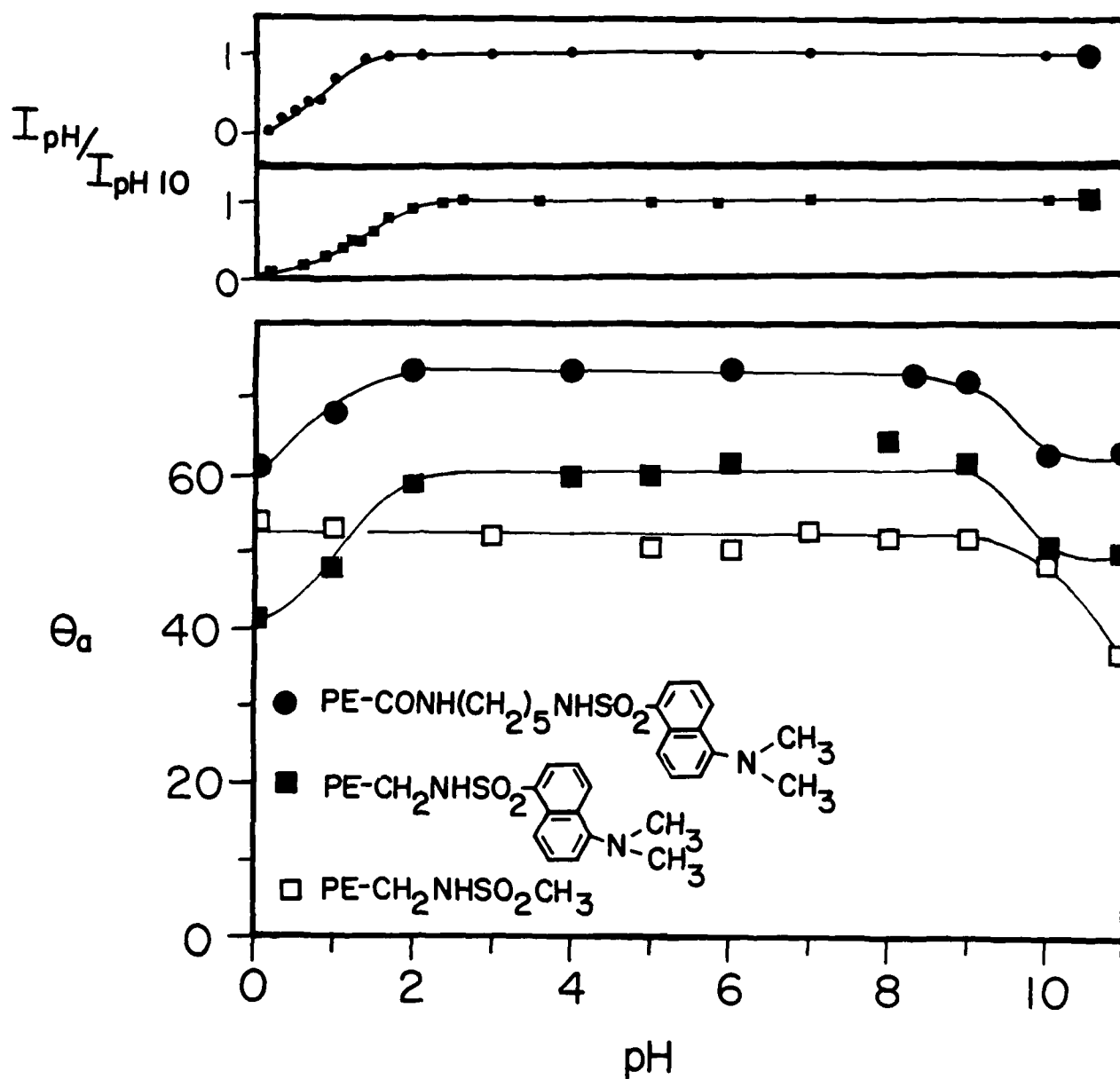


Figure 11. Advancing contact angle (θ_a) of water and intensity of fluorescence as a function of pH for PE-CONH(CH₂)₅NHSO₂-[2-(dimethylaminophenyl)]-1-naphthyl (●) and PE-CH₂NHSO₂-[2-(dimethylaminophenyl)]-1-naphthyl (■). The contact angle of PE-CH₂NHSO₂CH₃ (□) is shown for comparison.

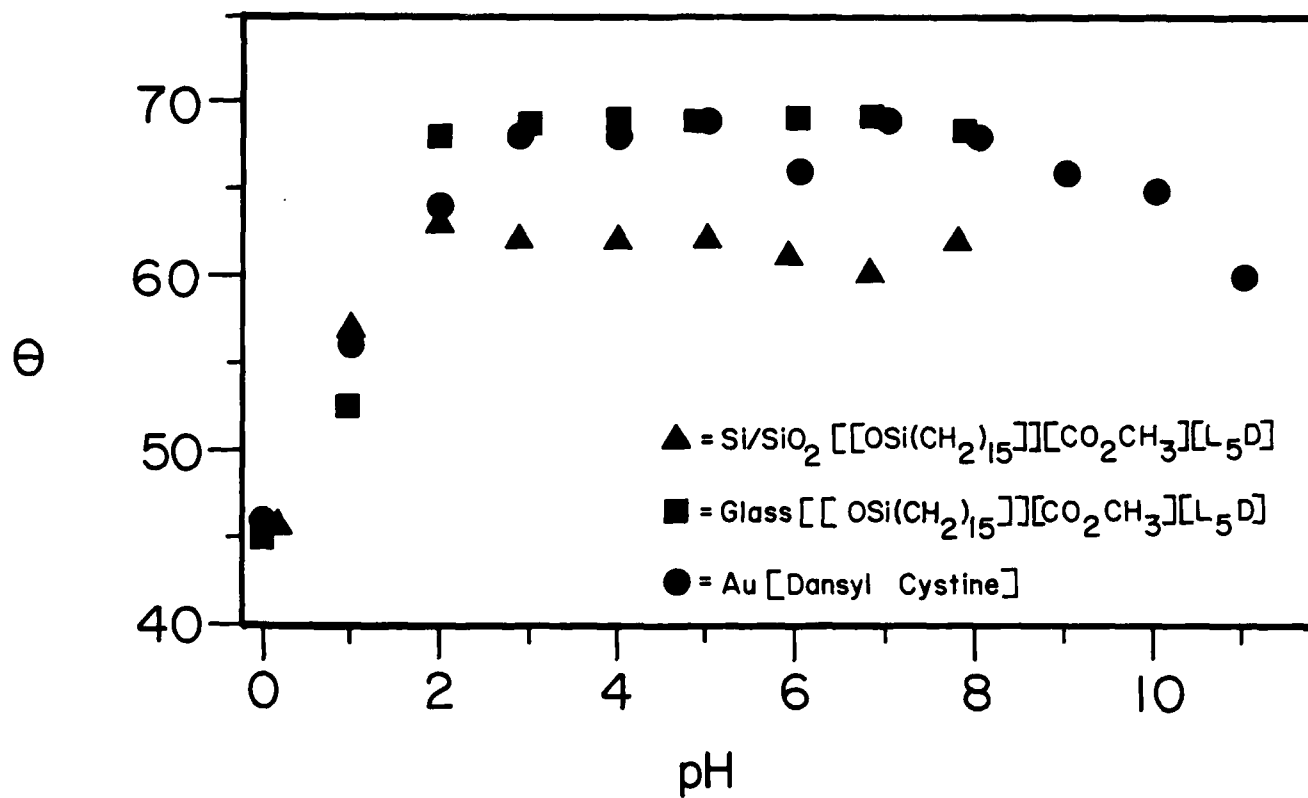


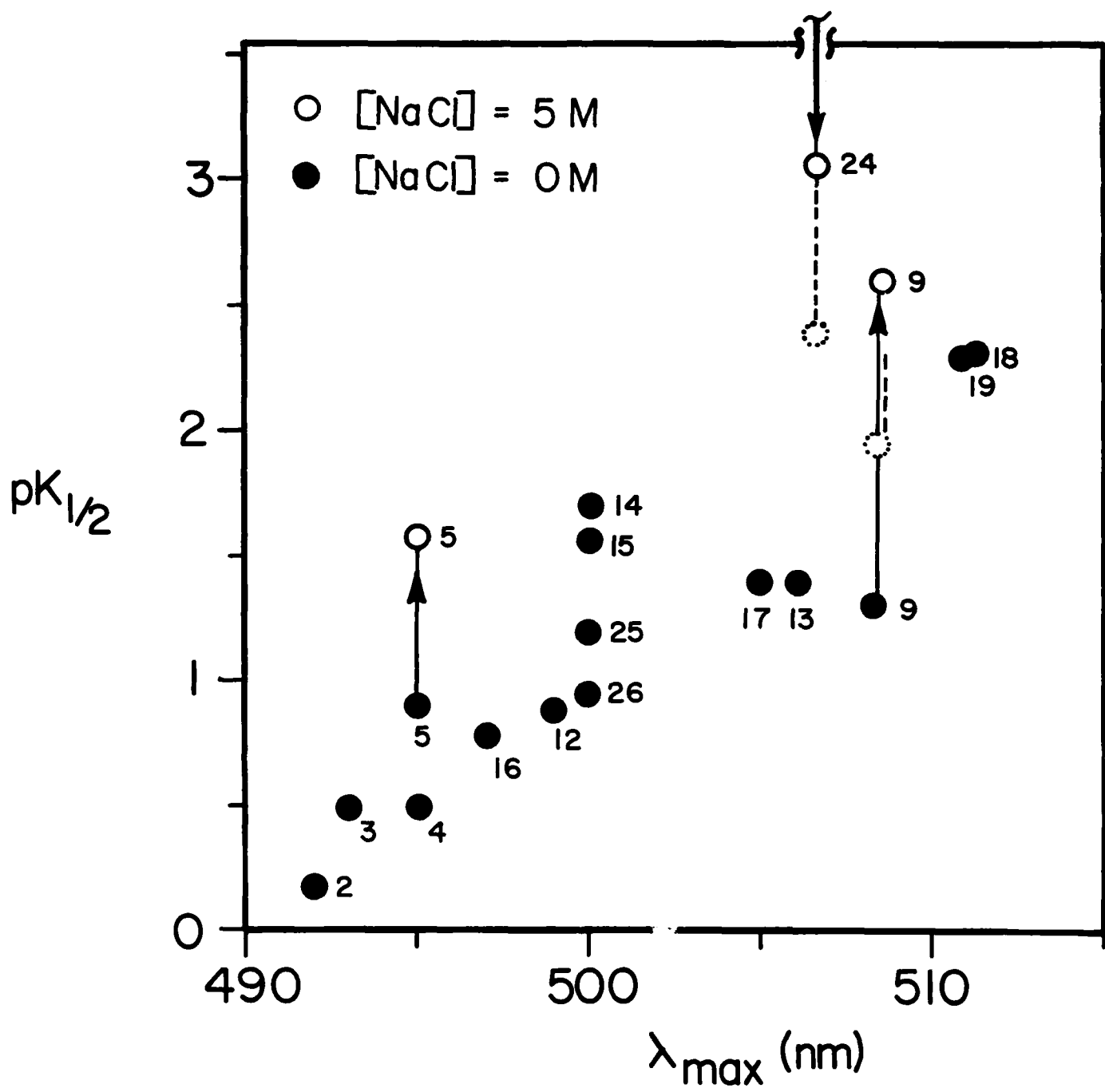
Figure 12. Advancing contact (θ) of water as a function of pH for three Dansyl-containing monolayers: \blacktriangle ,
Si/SiO₂ [[OSi(CH₂)₁₅] [CO₂CH₃] [L₅D]]; \blacksquare ,
Glass [[OSi(CH₂)₁₅] [CO₂CH₃] [L₅D]]; \bullet , Au [Dansyl cystine].

Salt Effects on Fluorescence. We ascribe the influence of the non-polar polymer substrate and of adjacent hydrophobic groups on the pH dependence of the fluorescence of the Dansyl group to their contribution to the low polarity of the environment in the vicinity of the Dansyl dimethylamino group, and to a resulting decrease in the basicity of this group. The less polar the environment of the Dansyl group, the lower its $pK_{1/2}$ and its value of λ_{max} . Figure 13 demonstrates that λ_{max} and $pK_{1/2}$ correlate well for all of the neutral Dansyl systems $PE[R_j][L_iD]$ listed in Table V.

Charged surfaces, on the other hand (especially negatively charged surfaces), do not follow the same correlation: Qualitatively, for materials in which the Dansyl group shares the interphase with a positively charged group ($PE[R^+][L_iD]$) the $pK_{1/2}$ of the Dansyl group is lower (that is, the Dansyl dimethylamino group is less basic) than expected on the basis of its λ_{max} ; for $PE[R^-][L_iD]$ the $pK_{1/2}$ is higher than expected from λ_{max} . On protonation, the dimethylamino group becomes positively charged. Charge-charge interactions involving Dansyl and adjacent groups in the interphase would provide one rationalization of the observed deviations. Alternatively, the presence of charged groups in the interphase might alter the local pH by "concentrating" or "repelling" protons at the interphase and generating a pH gradient between the interphase and the bulk solution. Regardless of the exact form of the rationalization, charge-charge interactions at the interphase would play a role in rationalizing the difference between the correlation of $pK_{1/2}$ and λ_{max} for neutral and charged samples of $PE[R^{+,-,0}][L_iD]$.

To determine the importance of charge-charge interactions in charged interphases, we compared the fluorescence titration curves for $PE[CO_2CH_3][L_5D]$ (neutral), $PE[CONHCH_2CH_2NH(CH_3)_2^+][L_5D]$ (positively charged) and

Figure 13. $pK_{1/2}$ as a function of λ_{\max} for various PE-D and monolayer surfaces for all neutral species in Table V (●). The numbers correspond to the entries in Table V. Data points are also shown for several surfaces (5, 9, 24) in 5 M NaCl (see text) as open symbols (○) attached by a line to the datum for the same surface without added salt (24 is off scale). Our estimates of the $pK_{1/2}$ for 9 and 24 in the absence of charge-charge interactions or salt effects are shown as dotted symbols (⋯). These were estimated by subtracting 0.7 (the effect of 5 M NaCl on neutral species) from the values of $pK_{1/2}$ obtained in 5 M NaCl.



PE[CONHCH₂CH₂SO₃⁻][L₅D] (negatively charged) at the relatively low salt concentrations used in obtaining the data in Table V (Figure 13) ($\mu \approx 0.01$ -0.05 M, H₂SO₄) and at high salt ($\mu = 5$ M, NaCl) (Figure 14). The influence of increased ionic strength on the fluorescence titration curves of both PE[CO₂CH₃][L₅D] and the soluble 2 is relatively small: $pK_{1/2}$ increased by ~ 0.7 . For PE[CONHCH₂CH₂NH(CH₃)₂⁺][L₅D], $pK_{1/2}$ increased by 1.3; for PE[CONHCH₂CH₂SO₃⁻][L₅D] it decreased by 1.5. The values of $pK_{1/2}$ and λ_{max} observed at high salt (2.6 and 508 nm and 3.1 and 508 nm respectively) fit reasonably well with the correlation of Figure 12. This apparent fit is even better if the effect due to high salt on neutral species is taken into account (Figure 12). Thus, it appears that a substantial contribution to the values of $pK_{1/2}$ observed in fluorescence titrations of Dansyl groups at charged interphases can be attributed to charge-charge interactions. The similarity in the shift in $pK_{1/2}$ for PE[CO₂CH₃][L₅D] and for (soluble) 2 with an increase in ionic strength suggests that charge-charge interactions are relatively unimportant in an interphase containing only neutral species in addition to Dansyl groups. We note, however, that at pH 1 the ionic strength of the bulk solution is $\mu \approx 0.1$ M, and many Coulomb interactions might be shielded.

Temperature Effects. Figure 15 shows the dependence of λ_{max} on temperature for 2 in several solvents, and for PE[CO₂CH₃][L₂D] in contact with water. The value of λ_{max} for 2 is independent of temperature; that for PE-D increases significantly with temperature. It thus appears that the interfacial region has a higher polarity at higher temperatures. Increased mobility of species in the interphase at higher temperature would lead to increased penetration of the interphase by water (that is, to increased swelling) and would rationalize the observed behavior.

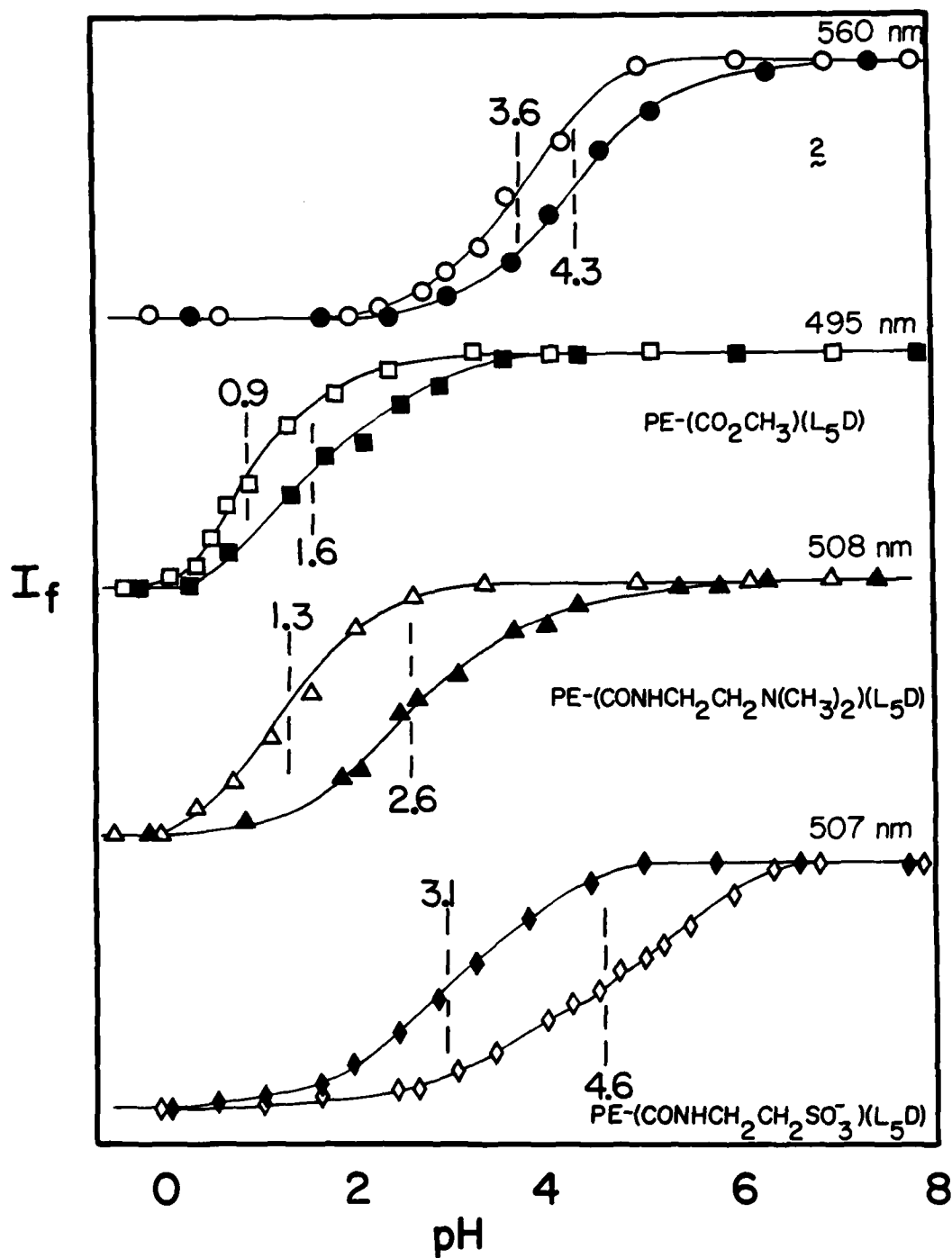


Figure 14. Intensity of fluorescence for 2 and several PE-D surfaces with neutral, positively charged, and negatively charged species as a function of pH in low salt (open symbols) and in 5 M NaCl (filled symbols). Values of $pK_{1/2}$ and of λ_{max} (pH 4) are indicated for each curve.

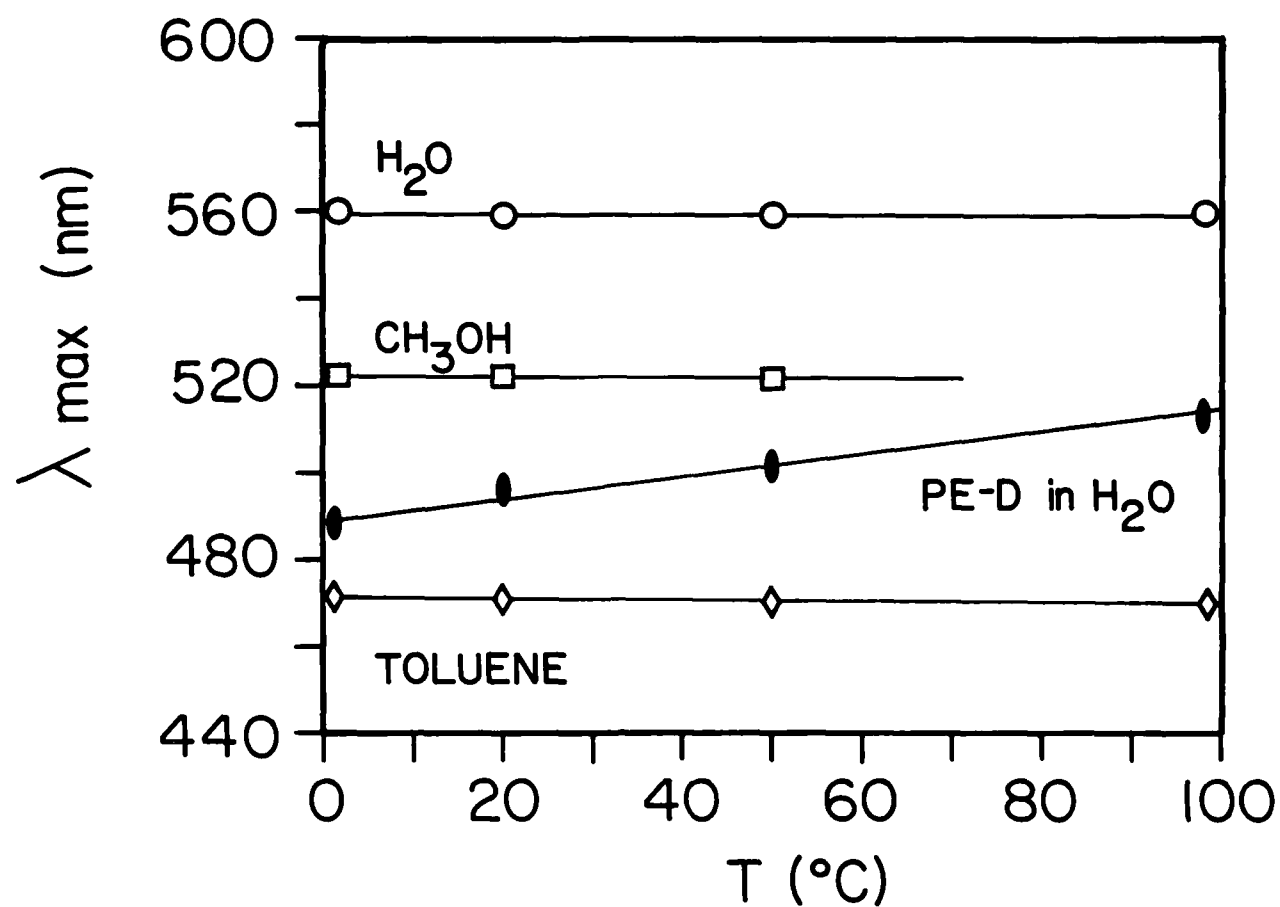


Figure 15. Fluorescence emission maximum of **2** (open symbols) in various solvents, and PE[CO₂CH₃][L₅Dansyl] in water (●) as a function of temperature.

Summary and Conclusions

We interpret the evidence summarized in this paper as indicating that the majority of the Dansyl groups present on PE-D experience a common environment that has a low polarity. The polarity of this environment is only weakly influenced by liquids in contact with the film. PE-D may contain a minority of Dansyl groups showing a higher sensitivity to liquid polarity, but the relatively small range observed for λ_{max} on changing solvent polarity, even for soluble derivatives of Dansyl, combined with the weak fluorescence characteristic of high polarity media, make it difficult to prove or disprove the existence of this hypothesized minority population. Thus, our conclusions concerning the Dansyl groups of the several PE-D systems examined are restricted to the easily-observed majority population.

The conclusions concerning the environment of the Dansyl groups of PE-D are based on two general types of evidence. First, fluorescence studies establish the homogeneity of the population of Dansyl groups, and the polarity of their environment. Second, correlations between changes in fluorescence intensity with pH and changes in contact angle with pH establish that the contact angle interphase contains a significant concentration of Dansyl groups, and that the acid-base behavior of these Dansyls is indistinguishable from that of the Dansyls giving rise to the greater part of the observed fluorescence. The contact angle interphase is thin--probably less than 10 Å. Thus, either most of the Dansyl groups of PE-D lie in the contact angle interphase, or the acid-base behavior of Dansyls in this interphase is very similar to that of Dansyls lying deeper below the surface. We cannot presently distinguish between these alternatives (see below).

We review in the following four points certain of the details supporting these conclusions, and conclude by outlining several remaining and continuing uncertainties.

1) The Dansyl groups of the simply functionalized derivatives of PE-CO₂H (e.g. PE[CO₂CH₃][L₂D]) experience a uniform environment. The width of the fluorescence peak for these materials is similar to that observed for model compounds in homogeneous solution; all Dansyl groups in the derivatives of polyethylene are quenched by aqueous acid, and the titration curve for fluorescence quenching is close to that expected for a single type of basic site.

2) The studies of fluorescence establish that the majority of Dansyl groups experience an environment having low polarity. This value, as judged by the position of λ_{\max} , corresponds to an effective dielectric constant of $\epsilon \sim 6-10$. The polarity of these Dansyl groups changes surprising little with solvent: the position of λ_{\max} is almost independent of solvent, and the intensity of fluorescence (a quantity which, in any event, is difficult to interpret as a measure of the environment) changes only slightly. The value of $pK_{1/2}$ for acidic quenching of fluorescence (a number indicating the solution pH required to protonate the dimethylamino group of the Dansyl moiety) is consistent with the polarity inferred from the observed values of λ_{\max} : this observation indicates that the low basicity of the dimethylamino group in functionalized polyethylene interphases containing only neutral groups in addition to Dansyl moieties is due to the low polarity of this interphase. The decrease in $pK_{1/2}$ on going from $\epsilon \sim 80$ in bulk water to $\epsilon \sim 9$ on PE[CO₂CH₃][L₅D] is about 3 pH units (3.6 to 0.8). This shift is very similar to that observed by Fernandez and Fromherz³¹ on transferring a

soluble, basic, coumarin dye from water to a dioxane/water mixture: In 82% dioxane ($\epsilon \approx 9.5$) the pK_a of this dye is ~ 3 pH units lower than in water.

3) The surface density of Dansyl groups is intermediate: they are close enough, on the average, that energy transfer (resulting in fluorescence depolarization) occurs rapidly; they are far enough apart that Coulomb interactions between the dimethylammonium groups of protonated Dansyl groups has little influence on $pK_{1/2}$ (as judged by the absence of the significant salt effect that is observed when Dansyl groups are mixed with charged species such as RSO_3^- and $RNH(CH_3)_2^+$ on the surface).

4) Dansyl groups occupy the contact angle interphase. Changes in the contact angle of aqueous solutions of different pH on Dansyl-derivatized polyethylene correlate with protonation of the dimethylamino moiety and deprotonation of the sulfonamide group. The magnitudes of the changes in contact angle with pH are similar to those observed in model surfaces based on silanized glass and silica, and gold functionalized with adsorbed disulfides. Thus, the density of Dansyl groups in the contact angle interphase of the polyethylene derivatives appears to be high.

These observations characterize the environment of the majority of Dansyl groups in PE-D. We believe that these groups are distributed in a thin functionalized interphase, but are not situated exclusively at the "surface" of the polymer: that is, in direct van der Waals contact with the liquid phase. If the Dansyl groups were on the surface, we would have expected greater sensitivity to ω_{max} and fluorescence intensity to solvent polarity.

The major uncertainty in the interpretation of these data thus concerns the question of a minority ("surface") population of Dansyl groups on PE-D. The fluorescence measurements do not have the resolution required to establish clearly a minority (solvent-sensitive) population against the background of a

majority (solvent-insensitive) population, but suggest the existence of such a population. Other studies (to be published) indicate clearly that functional groups lying below the contact angle interphase can still engage in proton transfer reactions with an aqueous solution in contact with these films. It seems physically reasonable that Dansyl groups located in direct contact with liquid should have different properties than Dansyl groups located deeper in the interphase. The correlation of acid quenching of fluorescence with contact angle indicates, however, that the acid-base behavior of the Dansyl groups in the contact angle interphase (that is, in direct contact with solvent) is indistinguishable from that of the majority population of Dansyl groups, which appears (on the basis of apparent polarity of its local environment) to be relatively isolated from solvent. We cannot presently reconcile these observations, and we will describe experiments designed to explore the properties of Dansyl groups located at different depths in the functionalized interphase of PE-D in subsequent papers.

Experimental Section

General Procedures. Fluorescence spectra were determined on a Perkin Elmer MPF-4 spectrofluorometer. Excitation was at 350 nm (20 nm excitation slit) with an added Corion P10-350-H-2638 filter (350 nm bandpass, 11 nm halfwidth) to eliminate stray light from the excitation beam. Spectra of films were determined in cuvettes with the film inserted diagonally. The positioning of the films can significantly influence the observed fluorescence intensity by changing the surface area exposed to the beam. For this reason the films were cut just enough larger than the diagonal length of the cuvette that the film was held in place by its own rigidity. Fluorescence intensities (I_f) were normally determined by integrating the area under the peaks observed and were not corrected for wavelength dependent variations in the detector sensitivity. When determining I_f as a function of pH for PE-D surfaces in aqueous solution it was found that the integrated area was directly proportional to the peak height (that is, that the peak shape was constant). Peak height was thus used to determine I_f in these cases. ATR-IR spectra were determined on a Perkin-Elmer Model 598 infrared spectrometer using a KRS-5 thallium bromide/iodide crystal. Values of pH were measured using a Cole Parmer 5995 pH meter with a Cole Parmer R5991-81 electrode. ESCA spectra were obtained on a Physical Electronics Model 548 spectrometer (MgK_{α} X-ray source, 50 eV pass energy, 10^{-8} to 10^{-9} torr). This instrument was calibrated according to ASTM STP 699. Spectra were quantified by the software supplied with the instrument using the integrated peak areas.

Contact Angle Measurements. Contact angles were determined on a Rame-Hart Model 100 contact angle goniometer equipped with an environmental chamber by estimating the tangent normal to the drop at the intersection between the sessile drop and the surface. These were determined 5-20 seconds after application of the drop. Though considered to be "advancing" angles, the drops maintained their contact angle with the surface for several hours ($\pm 2^\circ$) under the environmental conditions described below.³ Receding contact angles were 0° on all surfaces described in this paper. We believe this hysteresis is due to surface swelling.³ The humidity in the chamber was maintained at 100% by filling the wells in the sample chamber with distilled water. The temperature was not controlled and varied between 20 and 25 $^\circ\text{C}$. The volume of the drop used was always 1 μL . Polyethylene samples were cut to a size of 0.5 x 2 cm and attached by the back of the sample to a glass slide using two-sided Scotch tape to keep the sample flat. All reported values are the average of at least eight measurements taken at different locations on the film surface and have a maximum error of $\pm 3^\circ$. The pH profiles were fully reversible after rinsing the drops from the surface with distilled water and drying in air. The buffers used (0.05 M) were as follows: pH 1, 0.1 N HCl; pH 2, maleic acid; pH 3, tartaric acid; pH 4, succinic acid; pH 5, acetic acid; pH 6, maleic acid; pH 7 and pH 8, HEPES; pH 9 and pH 10, CHES; pH 11, triethylamine; pH 12, phosphate; pH 13, pH N NaOH.

Fluorescence Polarization. The fluorescence polarization was determined by the standard method from eq 2 using an Hitachi 018-0054 polarization attachment to the spectrofluorometer. All values were determined at 500 nm.

PE-CO₂H.³ Low-density polyethylene film (Flex-O-Film DRT-B-600, $\sim 50\text{ cm}^2$) was stirred in refluxing CH_2Cl_2 for 24 h to remove antioxidants and other soluble additives. After drying in vacuum for 18 h the film was oxidized by

floating it on a mixture of chromic acid ($\text{CrO}_3/\text{H}_2\text{O}/\text{H}_2\text{SO}_4$; 29/42/29) at 72 °C for 1 min and then rinsed 3 times in water, once in acetone and air dried. In all of the procedures listed below, "rinsing" of the polyethylene samples involved holding the corner of the sample with tweezers and gently moving the sample through the liquid (~100 mL) for 10-20 sec. After this manipulation the samples were allowed to soak in the liquid for 1-3 min before being removed from it.

~~PE-CO₂CH₃ and NaBH₄ treated PE-CO₂H~~ were made as described previously.³

~~H-L₂-Dansyl~~. Dansyl chloride (2 g, Sigma, 95%) was dissolved in 30 mL of CH_2Cl_2 . This solution was added to 50 mL of CH_2Cl_2 containing 30 mL of ethylenediamine. After stirring for 30 min the solution was rinsed 4 times with water. The organic portion was dried over MgSO_4 and the solvent was removed. The remaining solid was recrystallized from 3:2 toluene:cyclohexane. The solid melted at 150.5-151.5 °C (lit.³⁰ 149-151 °C); IR 3360, 1325, 1160 cm^{-1} ; ^1H NMR δ 2.7 (2 H, t, $-\text{CH}_2-$), 2.9 (10 H, m, $(\text{CH}_3)_2\text{-N}$, $-\text{CH}_2-$, $-\text{NH}_2$), 7.2 (1 H, d, Ar-H), 7.6 (2 H, m, Ar-H), 7.3 (2 H, m, Ar-H), 8.6 (1 H, d, Ar-H).

~~H-L₅-Dansyl~~ and ~~H-L₅(CO₂H)-Dansyl~~. Dansyl cadaverine (H-L₅-Dansyl) was obtained from Sigma and used as received. α -Dansyl-L-lysine (H-L₅(CO₂H)-Dansyl) was obtained from Chemical Dynamics Corp and used as received.

~~H-L₆-Dansyl~~. 1,6-Diaminohexane (MCB, 15.5 g) was dissolved in 150 mL of diethyl ether. To this solution was added 25 mL of diethyl ether containing 1 g of Dansyl chloride (Sigma). The yellow solution turned milky white in a few seconds. After 10 min of stirring the solution was rinsed with three 200-mL portions of water to remove excess amine. The ether solution was dried over anhyd MgSO_4 and the solvent was removed. The solid was not further purified or characterized, but was used directly in reaction with PE-COCl.

$\text{CH}_3\text{CONHCH}_2\text{CH}_2\text{NH-Dansyl}$ (2). Dansylamine (H-L₂-Dansyl, 0.5 g) was dissolved in 15 mL of CH_2Cl_2 containing 1 mL of triethylamine. Acetyl chloride (2 mL) was added and the mixture was stirred 10 min. The solution was extracted four times with 50-mL portions of pH 7 buffer ($\text{KH}_2\text{PO}_4/\text{KOH}$; Fisher buffer concentrate) and dried over anhyd MgSO_4 . The solvent was removed and the solid was recrystallized from water and dried. mp 102-103.5 °C; IR 3220, 1650, 1325, 1150 cm^{-1} ; ^1H NMR δ 1.8 (3 H, s, $\text{CH}_3\text{C=O}$), 2.9 (6 H, s, $(\text{CH}_3)_2\text{N}$), 3.1 (2 H, q, $-\text{CH}_2-$), 3.3 (2 H, q, $-\text{CH}_2-$), 5.6 (1 H, broad t, $-\text{SO}_2\text{NH}$), 6.0 (1 H, broad s, CONH), 7.2 (1 H, d, Ar-H), 7.6 (2 H, m, Ar-H), 8.3 (2 H, m, Ar-H), 8.6 (1 H, d, Ar-H).

H-L₁₂-Dansyl. Dansyl chloride (1 g, Sigma, 95%) was dissolved in 40 mL of THF. This solution was slowly added to a rapidly stirring solution of 100 mL of THF containing 0.63 g of 1,12-diaminododecane (Polysciences Inc.). Diethyl ether (200 mL) was added and the solution was rinsed with three 200-mL portions of 0.1 N NaOH followed by three 200-mL portions of pH 7 $\text{KH}_2\text{PO}_4/\text{KOH}$ buffer (Fisher concentrate). The ether portion was dried over anhyd MgSO_4 and the solvent was removed by evaporation. The residual solid was recrystallized from 1.0 N HCl, rinsed in water and dried in vacuo for 4 h (mp = 198.5-200 °C). As with H-L₆-Dansyl this solid was not further purified, but was used directly in reaction with PE-COCl.

PE-[CO₂R][L_iD]. PE-CO₂H was soaked in diethyl ether saturated with PCl_5 for 60 min. The film was removed and immediately immersed in 10 mL of anhydrous methanol containing 100 mg of H-L₅-D (Dansyl cadaverine) for 5 sec (in the case of $i = 2, 6$ or 12, or α -Dansyl-L-lysine, the amine hydrochloride may have been present, and 0.2 mL of triethylamine was added). The fluorescence intensity of the film was the same whether 10-100 mg of Dansyl derivative was used. The resulting film was then rinsed in CH_3OH twice and

water twice. This procedure results in the methyl ester surface $\text{PE}[\text{CO}_2\text{CH}_3][\text{L}_5\text{D}]$. In order to get accurate fluorescence intensity measurements in non-polar solvents, the residual PCl_5 in the film was destroyed by treating the film with $\text{NH}_4\text{OH}/\text{H}_2\text{O}$ (saturated) for 10 min. If this neutralization is not carried out, HCl released by reaction in the film of ambient water with PCl_5 protonates the surface Dansyl groups and quenches their fluorescence. In water or methanol, this fluorescence quenching does not appear to happen, perhaps because the system is buffered by the protic solvent. A brief survey showed no difference between NH_4OH treated and unreacted films except in non-polar solvents. Since, however, NH_4OH could react with surface esters this treatment was not routinely performed. Substituting ethanol or *n*-hexanol for methanol above resulted in $\text{PE}[\text{CO}_2\text{CH}_2\text{CH}_3][\text{LD}]$ and $\text{PE}[\text{CO}_2(\text{CH}_2)_5\text{CH}_3][\text{LD}]$ respectively.

$\text{PE}[\text{CO}_2\text{H}][\text{L}_5\text{D}]$. This material was made by the same method as used for $\text{PE}[\text{CO}_2\text{CH}_3][\text{L}_5\text{D}]$ except using acetone as a solvent instead of methanol. Alternatively this surface could be made by soaking $\text{PE}[\text{CO}_2\text{CH}_3][\text{L}_5\text{D}]$ in 1 N NaOH for 24 h. These two procedures gave films having similar properties in all tests performed.

$\text{PE}[\text{R}_j][\text{LD}]$. All of the mixed surfaces were made following the procedure given above for $\text{PE}[\text{CO}_2\text{CH}_3][\text{L}_5\text{D}]$, with H-R_j added to the Dansyl-containing methanol solution. R_1 : 26 mg, 200 mg and 1.0 g of $\text{NH}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ was added to achieve molar ratios of 1, 7.6 and 38 respectively. R_2 : 30 mg and 300 mg of octylamine was added to give molar ratios of 0.8 and 8 respectively. R_3 : 20 mg and 200 mg of 40% CH_3NH_2 in H_2O was added to give molar ratios of 0.9 and 8.6 respectively. R_4 : 200 μL of 29% NH_3 in H_2O was added to give a molar ratio of ~ 12 . (This surface could also be made by allowing $\text{PE}[\text{CO}_2\text{CH}_3][\text{L}_5\text{D}]$ to react with $\text{NH}_4\text{OH}/\text{H}_2\text{O}$ (saturated) for several days at room temperature.) R_5 :

10 mg, 20 mg, 30 mg, 50 mg and 150 mg of ethanolamine was added to give molar ratios of 0.55, 1.65, 2.7 and 8.2 respectively. Adding 500 mg, molar ratio = 27, yielded a nonfluorescent surface. R_6 : 1.0 mL and 2 mL of 1 M taurine adjusted to pH 10 with NaOH was added to give molar ratios of 3.4 and 6.7 respectively. Performing the same reaction (1 mL of taurine) with the Dansyl reduced to 10 mg and 1.8 mg gave molar ratios of 34 and 189 respectively. Alternatively 1.25 g of taurine and 1.5 mL of triethylamine were added to the standard Dansyl/ CH_3OH solution to give a molar ratio of 34. The two surfaces with a molar ratio of 34 seemed similar.

PE-CH₂NH-Dansyl. PE-CO₂H was treated with PCl_5 in diethyl ether for 1 h followed by $\text{NH}_4\text{OH}/\text{H}_2\text{O}$ (saturated) for 10 min to form PE-CONH₂. Evidence for the correctness of this structure comes from the ATR-IR spectra. The amide carbonyl (1660 cm^{-1}) and NH (1550 cm^{-1}) are clearly seen; the CO₂H peak at 1710 cm^{-1} has largely disappeared; and at pH 13 no new CO₂⁻ peak (1560 cm^{-1}) appears. After rinsing with water three times and drying in air the amide was reduced in 200 mL of diethyl ether containing 1 g of LiAlH_4 by refluxing the solution for 18 h. The film was rinsed twice in conc. HCl and twice in water to form PE-CH₂NH₂. This film was put into 5 mL of 1 M Dansyl chloride (Sigma) in acetone for 5 sec. To this reaction mixture was added 2 mL of aqueous Na_2CO_3 (saturated); the reaction was stirred for 30 sec. The film was removed, rinsed 3 times in water, twice in methanol and air dried.

PE-CO₂NHCH₂CH₂NH-Dansyl. PE-CO₂H was esterified in 500 mL of CH_3OH containing 75 mL H_2SO_4 at 40 °C for 18 h to form PE-CO₂CH₃. After rinsing with methanol and air drying the film was soaked in neat $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ for 1 week at room temperature. After rinsing with methanol three times this film was treated with Dansyl chloride as above.

$\text{PE-CH}_2\text{NHSO}_2\text{CH}_3$. $\text{PE-CH}_2\text{NH}_2$ was treated for 1 min with 5 mL of neat $\text{CH}_3\text{SO}_2\text{Cl}$ to which had been added very carefully 1 mL of triethylamine. The film was rinsed several times in water, once in methanol and air dried.

$\text{Si/SiO}_2[[\text{OSi}(\text{CH}_2)_{15}]][\text{CO}_2\text{CH}_3][\text{L}_5\text{D}]$. Silicon wafers (Monsanto, cut to 1.4 cm x 4 cm) were cleaned in 1:1 $\text{H}_2\text{SO}_4/30\% \text{H}_2\text{O}_2$ at 70 °C for 1 h. After rinsing in distilled water the wafer was allowed to react with $\text{CH}_2=\text{CH}(\text{CH}_2)_{15}\text{SiCl}_3$ (~1%, w:w) in hexadecane for 1 h. After rinsing (10 mL of each solvent poured over the wafer three times) in hexane and ethanol the surface was oxidized in a solution containing 0.5 mM potassium permanganate, 19.5 mM potassium periodate, and 1.8 mM K_2CO_3 (pH 7.5) for 18 h at 20 °C. The reaction was quenched by dipping the slide into aqueous sodium bisulfite solution (30 g/L), rinsing in water, 0.1 N HCl, water and ethanol. Dansyl cadaverine was then attached as for $\text{PE-CO}_2\text{H}$.

$\text{Glass}[[\text{OSi}(\text{CH}_2)_{15}]][\text{CO}_2\text{CH}_3][\text{L}_5\text{D}]$. Glass was substituted for silicon in the reactions above to form this surface.

$\text{Au}[\text{Dansyl cystine}]$. Dansyl cystine (Sigma) was dissolved in ethanol (10 mg in 5 mL) and allowed to adsorb onto a freshly evaporated gold surface for 18 h. The surface was then rinsed twice (by pouring 50 mL of ethanol over the surface) and air dried.

Assay of the Surface Density of Dansyl Groups by Hydrolysis.

$\text{PE}[\text{CO}_2\text{CH}_3][\text{L}_5\text{D}]$ was treated in acid to hydrolyze the amide bond to allow the surface groups to be counted. To these strips (2 and 4 cm², 4 each) was added 200 µL of H_2O and 800 µL of 50% (v/v) $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$. As a control, three strips of unoxidized polyethylene (3 cm² each) were treated in the PCl_5 /ether and Dansyl/methanol solutions and subjected to the same hydrolysis conditions. For standards a solution of Dansyl cadaverine was made up to 100 mg/L and serially diluted by half to 0.2 mg/L. To 200 µL of each of these standards

was added 800 μL of the 50% H_2SO_4 . All of the samples were heated to 100 $^\circ\text{C}$ for 18 h in test tubes sealed with rubber septa. The tubes were made basic with 4 N NaOH (4 mL) followed by 5 mL of H_2O . The hydrolysis products in each tube were extracted into 5 mL of methylene chloride and the fluorescence intensity was determined at 510 nm (excitation 350 nm, 14 nm excitation slit, 10 nm emission slit). The result for the eight samples was determined to be $6.2 \times 10^{14} \text{ cm}^{-2}$ by comparison with the intensity of the standards. The control films (unoxidized) were below the lowest standard with a resulting coverage $< 2 \times 10^{13} \text{ dm}^{-2}$, or $< 4\%$ of the oxidized film.

Notes and References

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Captions

Scheme I. Reactions Used to Modify the Surface of Polyethylene. The schematic structures for $PE[R_2][L_5D]$ suggest the range of groups present in the functionalized interphase, and illustrate the nomenclature used for these materials.

Scheme II. Organic Monolayer Films Used to Provide Models for PE-D.

Figure 1. ATR-IR spectra of the carbonyl region of $PE-CO_2H$ and derivatives. The frequencies indicated are those used in identifying the carbonyl-containing functional groups of major interest: carboxylic acid and ketone (1710 cm^{-1}); methyl ester (1740 cm^{-1}); carboxylate ion (1560 cm^{-1}); and amide (1660 cm^{-1}). The spectrum labeled $PE-H; PCl_5; CH_3OH$ is a control demonstrating that polyethylene that has not been oxidatively functionalized does not develop carbonyl functionality using the succession of treatments used to convert $PE-CO_2H$ to $PE-COCl$ and thence to $PE-CO_2CH_3$. The spectra taken at pH 13-14 and used to identify free carboxylic acid groups on the basis of the characteristic shift between CO_2H and CO_2^- were obtained with procedures outlined previously.³

Figure 2. Fluorescence emission spectra of: upper, Z in solution in representative solvents; lower, $PE[CO_2H][L_5D]$ in contact with the same solvents. For all samples the exciting frequency was 350 nm. Solution spectra were determined at $1.5 \times 10^{-5}\text{ M}$.

- Figure 3. Fluorescence emission maxima for $\tilde{2}$ (○) and $\text{PE}[\text{CO}_2\text{H}][\text{L}_5\text{Dansyl}]$ (●) as a function of solvent dielectric constant (data from Table III). The excitation wavelength for all samples was 350 nm. Solutions were 1.5×10^{-5} M (except cyclohexane, in which the probe was much less soluble). All soluble samples (except that in cyclonexane) had adsorption $\approx 0.061 \pm 0.001$ at 350 nm.
- Figure 4. Fluorescence intensity (relative quantum yield, I_f) for $\tilde{2}$ (○) and $\text{PE}[\text{CO}_2\text{H}][\text{L}_5\text{Dansyl}]$ (●) as a function of solvent dielectric constant (data from Table III).
- Figure 5. Fluorescence polarization P (eq 2) of $\tilde{2}$ (○) and $\text{PE}[\text{CO}_2\text{CH}_3][\text{L}_5\text{D}]$ (●) in solvents with various values of viscosity η at the temperatures indicated. The units of η are cp.
- Figure 6. Emission maximum as a function of pH for several PE-D surfaces (with carboxylic acid groups in the linking group L, with carboxylic acid groups on the surface and in L, and with no carboxylic acid groups) and for the soluble models $\tilde{2}$ and $\tilde{3}$. The emission maxima in methanol are also shown for comparison.
- Figure 7. Emission maximum as a function of pH for PE-D surfaces with acidic, basic and neutral surface species and for the soluble models $\tilde{1}$ and $\tilde{2}$. The emission maxima in methanol are also shown for comparison.
- Figure 8. Fluorescence intensity as a function of solution pH for several PE-D samples. Also shown is $\tilde{2}$ in water (1.5×10^{-5} M). The values of solution pH required to reduce the fluorescence intensity by one-half (the $\text{pK}_{1/2}$) are indicated by dashed lines. The emission maximum for each surface at pH = 4 is given on the right-hand side of each curve.

Figure 9. Fluorescence intensity as a function of pH for $\text{PE}[\text{CO}_2\text{CH}_3][\text{CONHCH}_2\text{CH}_2\text{SO}_3^-][\text{L}_5\text{D}]$ with various ratios of taurine/Dansyl in the reaction mixture (\circ , 0; \bullet , 3.4; \blacklozenge , 34; \blacksquare , 189).

Figure 10. Fluorescence intensity as a function of pH for $\text{PE}[\text{CONHCH}_2\text{CH}_2\text{OH}][\text{CO}_2\text{CH}_3][\text{L}_5\text{D}]$ with various ratios of ethanolamine/Dansyl in the reaction mixture (\circ , 0; \bullet , 0.5; \bullet , 1.7; \blacksquare , 2.7; \blacklozenge , 8.2). A surface was made with a molar ratio of 27 but the fluorescence was too weak to permit an accurate determination of the $\text{pK}_{1/2}$.

Figure 11. Advancing contact angle (θ_a) of water and intensity of fluorescence as a function of pH for $\text{PE}[\text{CO}_2\text{CH}_3][\text{L}_5\text{D}]$ (\bullet) and $\text{PE}-\text{CH}_2\text{NH}-\text{Dansyl}$ (\blacksquare). The contact angle of $\text{PE}-\text{CH}_2\text{NHSO}_2\text{CH}_3$ (\square) is shown for comparison.

Figure 12. Advancing contact (θ) of water as a function of pH for three Dansyl-containing monolayers: \blacktriangle , $\text{Si}/\text{SiO}_2[[\text{OSi}(\text{CH}_2)_{15}][\text{CO}_2\text{CH}_3][\text{L}_5\text{D}]$; \blacksquare , $\text{Glass}[[\text{OSi}(\text{CH}_2)_{15}][\text{CO}_2\text{CH}_3][\text{L}_5\text{D}]$; \bullet , $\text{Au}[\text{Dansyl cysteine}]$.

Figure 13. $pK_{1/2}$ as a function of λ_{\max} for various PE-D and monolayer surfaces for all neutral species in Table V (●). The numbers correspond to the entries in Table V. Data points are also shown for several surfaces (5, 9, 24) in 5 M NaCl (see text) as open symbols (○) attached by a line to the datum for the same surface without added salt (24 is off scale). Our estimates of the $pK_{1/2}$ for 9 and 24 in the absence of charge-charge interactions or salt effects are shown as dotted symbols (⋯). These were estimated by subtracting 0.7 (the effect of 5 M NaCl on neutral species) from the values of $pK_{1/2}$ obtained in 5 M NaCl.

Figure 14. Intensity of fluorescence for 2 and several PE-D surfaces with neutral, positively charged, and negatively charged species as a function of pH in low salt (open symbols) and in 5 M NaCl (filled symbols). Values of $pK_{1/2}$ and of λ_{\max} (pH 4) are indicated for each curve.

Figure 15. Fluorescence emission maximum of 2 (open symbols) in various solvents, and PE[CO₂CH₃][L₅Dansyl] in water (●) as a function of temperature.

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